MODELS AND DESIGNS FOR GENERALIZATIONS OF MIXTURE EXPERIMENTS WHERE THE RESPONSE DEPENDS ON THE TOTAL AMOUNT

BY

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To Polly

and

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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The definition of a mixture experiment requires that the response depend only on the proportions of the components present in the mixture and not on the total amount of the mixture. This definition is extended to encompass experiments where the response may also depend on the total amount of the mixture. Experiments of this type are referred to as general mixture experiments.

Three types of general mixture experiments (mixture-amount, component amount, and component-wise mixture) are discussed. Designs and models for these experiments are presented and compared.

A mixture-amount experiment consists of a series of usual mixture experiments conducted at each of two or more

levels of total amount. Mixture-amount models are developed by writing the parameters of mixture models as functions of the total amount. This class of models is quite broad in that it includes models that are appropriate when the components blend differently at the different levels of total amount as well as models that are appropriate when the effect of the total amount is not the same with all component blending properties. Designs for both unconstrained and constrained mixture-amount experiments are discussed, as are techniques for fractionating mixture-amount designs.

Component amount experiments utilize standard response surface designs and polynomial models in the component amounts. Component-wise mixture experiments are similar to usual mixture experiments, except that the level of total amount is not fixed and therefore may have an effect on the response. Component-wise mixture models and designs can be specified in terms of the component amounts or in terms of component-wise proportions.

Several real and hypothetical examples are utilized to illustrate and compare the mixture-amount, component amount, and component-wise mixture designs and models. Recommendations are given as to when each of the three experimental approaches should be used.

CHAPTER ONE
INTRODUCTION

1.1 The Response Surface Problem

In a general response surface problem, interest centers around an observable response y which is a function of q predictor variables $x_1, x_2, \ldots, x_q$. The predictor variables are quantitative and continuous and their values are assumed to be controlled by the experimenter. The response y is quantitative and continuous. The functional relationship between the predictor variables and the response may be expressed as

$$y_k = f(x_{k1}, x_{k2}, \ldots, x_{kq}) + \varepsilon_k, \quad k=1,\ldots, N, \tag{1.1}$$

where y_k is the kth of N observations of the response in an experiment, x_{ki} is the value of the ith predictor variable for the kth observation, and ε_k is the experimental error contained in the kth observation.

The form of the function f in (1.1) is usually not known and may be quite complex. In practice, an approximating function is identified with as simple a form as possible; often first or second-degree polynomials in the predictor variables $x_1, x_2, \ldots, x_q$ are adequate. The selection of an appropriate approximating function (often

referred to as model selection) is the first step in solving a response surface problem. Usually a model linear in the parameters is chosen.

A linear response surface model may be written in matrix notation as

$$\underset{\sim}{y} = X\underset{\sim}{\beta} + \underset{\sim}{\varepsilon} , \tag{1.2}$$

where $\underset{\sim}{y}$ is an Nx1 vector of observed response values, X is an Nxp matrix of known constants ($N \geq p \geq q$), $\underset{\sim}{\beta}$ is a px1 vector of unknown parameters, and $\underset{\sim}{\varepsilon}$ is an Nx1 vector of random errors. It is usually assumed that $E(\underset{\sim}{\varepsilon}) = \underset{\sim}{0}$ and $Var(\underset{\sim}{\varepsilon}) = \sigma^2 V$, where V is a diagonal matrix. Most often in practice $V = I_N$ (the NxN identity matrix containing ones on the main diagonal and zeros elsewhere). Since $E(\underset{\sim}{\varepsilon}) = \underset{\sim}{0}$, the model (1.2) can alternately be expressed as

$$\underset{\sim}{\eta} = E(\underset{\sim}{y}) = X\underset{\sim}{\beta} . \tag{1.3}$$

Another step in solving the response surface problem is to estimate the parameters $\underset{\sim}{\beta}$ and refine the model form if necessary. If we assume $Var(\underset{\sim}{\varepsilon}) = \sigma^2 I_N$, then the ordinary least squares estimator of $\underset{\sim}{\beta}$ is given by

$$\underset{\sim}{\hat{\beta}} = (X'X)^{-1}X'\underset{\sim}{y} , \tag{1.4}$$

and has variance

$$\text{Var}(\hat{\underset{\sim}{\beta}}) = (X'X)^{-1}\sigma^2 \ . \tag{1.5}$$

The portion of response surface analysis involving model selection, parameter estimation, and model refinement is known as <u>regression analysis</u>. Hence, the model parameters are called <u>regression coefficients</u> and the response surface model is called the <u>regression model</u>.

Once a fitted regression model $\hat{\underset{\sim}{y}} = X\hat{\underset{\sim}{\beta}}$ is obtained, the next step is to test it for adequacy of fit. If it is found to be adequate, it can then be used to make predictions of expected response values for any set of predictor variable values $x_1, x_2, \ldots, x_q$ within the experimental region. If we let $\underset{\sim}{x}_0$ represent this set of values expanded to resemble the terms in the model, the predicted value and its variance for the expected mean response at $\underset{\sim}{x}_0$ are

$$\hat{y}(\underset{\sim}{x}_0) = \underset{\sim}{x}_0' \hat{\underset{\sim}{\beta}} \tag{1.6}$$

and

$$\begin{aligned} \text{Var}[\hat{y}(\underset{\sim}{x}_0)] &= \text{Var}(\underset{\sim}{x}_0' \hat{\underset{\sim}{\beta}}) \\ &= \underset{\sim}{x}_0'(X'X)^{-1}\underset{\sim}{x}_0 \sigma^2 \ . \end{aligned} \tag{1.7}$$

Under the assumption $\text{Var}(\underset{\sim}{\varepsilon}) = \sigma^2 V$ (where V is a known diagonal matrix, not necessarily the identity matrix), $\underset{\sim}{\beta}$ is estimated by weighted least squares, yielding

$$\hat{\underset{\sim}{\beta}} = (X'V^{-1}X)^{-1}X'V^{-1}\underset{\sim}{y} , \tag{1.8}$$

$$\mathrm{Var}(\hat{\underset{\sim}{\beta}}) = (X'V^{-1}X)^{-1}\sigma^2 , \tag{1.9}$$

and

$$\mathrm{Var}[\hat{y}(\underset{\sim}{x}_0)] = \underset{\sim}{x}_0'(X'V^{-1}X)^{-1}\underset{\sim}{x}_0\,\sigma^2 . \tag{1.10}$$

For more details on these formulas and regression analysis in general, see Draper and Smith (1981) or Montgomery and Peck (1982).

Note that the parameter estimators, parameter estimator variances, and prediction variances in (1.4) through (1.10) all depend on the Nxp matrix X, which is referred to as the (expanded) design matrix. Clearly the experimental design chosen is of great importance in determining the fitted model and its properties. Box and Draper (1975) gave 14 criteria to consider in choosing a response surface design. Myers (1971) presented several classes of response surface designs which support the fitting of first and second-degree polynomial models in the predictor variables. Among the designs discussed by Myers are the 2^q and 3^q factorials, the 2^{q-k} fractional factorials, and the central composite designs.

In recent years, computer-aided design of response surface experiments has received much attention. A design criterion of interest is chosen and points are selected for

the design from a candidate list so as to optimize the design criterion selected. Several design criteria of interest are:

1. D-optimality seeks to maximize $\det(X'X)$ or equivalently minimize $\det[(X'X)^{-1}]$.
2. G-optimality seeks to minimize the maximum prediction variance over a specified set of design points.
3. V-optimality seeks to minimize the average prediction variance over a specified set of design points.
4. A-optimality seeks to minimize trace $[(X'X)^{-1}]$.

Designs consisting of N points obtained by using these optimality criteria are referred to as D_N, G_N, V_N, and A_N-optimal designs. These design criteria and computer programs for implementing them are discussed by St. John and Draper (1975), Mitchell (1974), and Welch (1984).

In summary, the major parts of a response surface analysis are:

1. Selection of an appropriate model to approximate the response surface over the region of interest.
2. Development of a design which supports the fitting of the selected model form and provides for testing the adequacy of fit of the model.
3. Fitting the chosen model, testing it for adequacy of fit, and revising the model if necessary.
4. Determination of the levels or ranges of the predictor variables that yield the optimum response value.

In the following chapters, we will be concerned mainly with the first two items listed above, that is, model selection and design development.

1.2 Mixture Experiments--An Introduction

A mixture experiment involves mixing two or more components (ingredients) together to form some end product, and then measuring or observing one or more properties of the resulting mixture or end product. In the usual definition of a mixture experiment (Cornell 1981, Scheffé 1958), the properties of the mixture are assumed to depend on the proportions of the components present and not on the total amount of the mixture. Some examples of mixture experiments are:

1. Sandwich fish patties made using mullet, sheepshead, and croaker (Cornell and Deng 1982). The texture of the fish patties was one of several responses of interest.

2. Coatings (paints) made from blending a prime pigment, vehicle, and two extender pigments (Hesler and Lofstrom 1981). Hiding power and scrubbability were the properties of interest.

3. Waste glasses obtained by mixing SiO_2, B_2O_3, Al_2O_3, CaO, MgO, Na_2O, ZnO, TiO_2, Cr_2O_3, Fe_2O_3, and NiO (Chick, Piepel, Mellinger et al. 1981). Leach rates, viscosity, conductivity, and crystallinity were several of the glass properties investigated.

A mixture experiment problem is clearly a response surface

problem, with the proportions of the components in a mixture being the predictor variables.

In a mixture experiment (as defined above), the response to a mixture of q components is a function of the proportions $x_1, x_2, \ldots, x_q$ of components in the mixture. Since x_i represents the proportion of the ith component in the mixture, the following constraints hold:

$$0 \leq x_i \leq 1 \ (i=1,2,\ldots,q); \quad \sum_{i=1}^{q} x_i = 1 \ . \tag{1.11}$$

Mixture experiments having only these constraints are referred to as <u>unconstrained</u> mixture experiments. Physical, theoretical, or economic considerations often impose additional constraints in the form of lower and upper bounds on the levels of components

$$0 \leq L_i \leq x_i \leq U_i \leq 1 \quad (i=1,2,\ldots,q) \ . \tag{1.12}$$

Experiments where these additional constraints are imposed on the x_i are referred to as <u>constrained</u> mixture experiments.

The region of mixture component combinations defined by constraints (1.11) and (1.12) is referred to as the <u>constraint region</u>. Geometrically, restriction (1.11) defines the constraint region as a regular (q-1)-dimensional simplex. In general, restrictions (1.12) reduce the constraint region given by (1.11) to an irregular

(q-1)-dimensional hyperpolyhedron. For further discussion of the geometry of mixture experiments, see Crosier (1984) and Piepel (1983).

In constrained mixture experiments, it is often desirable (see Kurotori 1966, Gorman 1970, St. John 1984, Crosier 1984) to transform the components to new variables referred to as pseudocomponents. If at least one component has a nonzero lower bound, then the pseudocomponent values x_i' may be obtained from the original component values x_i by

$$x_i' = \frac{x_i - L_i}{1 - \sum_{j=1}^{q} L_j}, \quad i = 1,2,\ldots,q, \tag{1.13}$$

where $\sum_{j=1}^{q} L_j < 1$. Crosier (1984) referred to this as the L-pseudocomponent transformation. If at least one variable has a nonunity upper bound, then pseudocomponent values may be obtained by the U-pseudocomponent transformation,

$$x_i' = \frac{U_i - x_i}{\sum_{j=1}^{q} U_j - 1}, \quad i = 1,2,\ldots,q, \tag{1.14}$$

where $\sum_{j=1}^{q} U_j > 1$. Crosier (1984) presented additional discussion on the use of these two pseudocomponent transformations and gave guidelines for choosing between them.

Models and designs for mixture experiments are reviewed in Chapter 2. Before proceeding to that material, however, the purpose and subject of this research is presented.

1.3 The Subject of This Research--Generalizations and Extensions of Mixture Experiments

The purpose of this research is to consider extensions and generalizations of the usual mixture experiment described in Section 1.2. As a first step, the following general definition is presented.

> Definition: A general mixture experiment is an experiment in which two or more components (ingredients) are mixed together and a property (response) of the resulting mixture is measured. The response is assumed to be a function of the proportions of the components present in the mixture and possibly the total amount of the mixture.

The usual mixture experiment, as defined in Section 1.2, is obviously a special case of the general mixture experiment, where the total amount of the mixture does not affect the response. It will be seen in the following chapters that several quite different types of experiments also satisfy the definition of a general mixture experiment. Models and designs for these situations will be presented, discussed, and compared.

Models and designs for usual mixture experiments and mixture experiments with process variables form the basis for much of the work to follow. These topics are reviewed in Chapter 2.

CHAPTER TWO
LITERATURE REVIEW--MIXTURE AND MIXTURE-PROCESS VARIABLE EXPERIMENTS

This chapter reviews models and designs for (usual) mixture experiments and for mixture experiments with process variables.

2.1 Models for Mixture Experiments

Scheffé (1958) developed canonical forms of polynomial models for mixture experiments by substituting the mixture constraint $\sum_{i=1}^{q} x_i = 1$ into certain terms in the standard polynomial models and then simplifying. For example, with $q = 2$ mixture components, the standard second-degree polynomial model is

$$\eta = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_{12} x_1 x_2 + \alpha_{11} x_1^2 + \alpha_{22} x_2^2 . \qquad (2.1)$$

Multiplying the constant term by unity and applying the mixture restriction $x_1 + x_2 = 1$ to the x_i^2 terms yields $\alpha_0 = \alpha_0(x_1 + x_2)$, $x_1^2 = x_1(1 - x_2)$ and $x_2^2 = x_2(1 - x_1)$. Hence, (2.1) can be reduced to the form

$$\eta = \beta_1 x_1 + \beta_2 x_2 + \beta_{12} x_1 x_2 , \qquad (2.2)$$

where $\beta_1 = \alpha_0 + \alpha_1 + \alpha_{11}$, $\beta_2 = \alpha_0 + \alpha_2 + \alpha_{22}$, and $\beta_{12} = \alpha_{12} - \alpha_{11} - \alpha_{22}$.

The general forms of the first, second, and third-degree canonical polynomial models in q mixture components are

$$\eta = \sum_{i=1}^{q} \beta_i x_i \ , \tag{2.3}$$

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} x_i x_j \ , \tag{2.4}$$

and

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} x_i x_j + \sum_{i<j}^{q} \sum \delta_{ij} x_i x_j (x_i - x_j) + \sum_{i<j<k}^{q} \sum \beta_{ijk} x_i x_j x_k \ . \tag{2.5}$$

The special-cubic canonical polynomial model is a reduced form of the full cubic model (2.5) obtained by deleting the $\delta_{ij} x_i x_j (x_i - x_j)$ terms.

In each of the above model forms, the first q terms, $\beta_1 x_1 + \ldots + \beta_q x_q$, represent the linear blending of the components while the remaining terms represent nonlinear blending of the components. We shall refer to these phenomena throughout, as the linear and nonlinear blending properties of the components.

Scheffé's canonical polynomial models are widely used and have been shown to adequately approximate many types of

mixture response surfaces. However, there are certain types of mixture surfaces for which the canonical polynomial models are not adequate. For example, when one or more of the mixture components have an additive effect, Becker (1968) recommended that homogeneous models of degree one be used. [A function $f(x,y, \ldots ,z)$ is homogeneous of degree n if $f(tx,ty, \ldots ,tz) = t^n f(x,y, \ldots ,z)$ for every $t > 0$.] Three such models, which Becker referred to as H1, H2, and H3, are given by

$$\text{H1:}\quad \eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} \min(x_i,x_j) + \ldots + \beta_{12\ldots q} \min(x_1,x_2,\ldots,x_q) , \tag{2.6}$$

$$\text{H2:}\quad \eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} x_i x_j/(x_i+x_j)^{2-1} + \ldots + \beta_{12\ldots q} x_1 x_2 \ldots x_q/(x_1+x_2+\ldots+x_q)^{q-1}, \tag{2.7}$$

$$\text{H3:}\quad \eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} (x_i x_j)^{1/2} + \ldots + \beta_{12\ldots q} (x_1 x_2 \ldots x_q)^{1/q} . \tag{2.8}$$

If the denominator of a term in H2 is zero, that term is defined to be zero. In practice, the second-order forms of H1, H2, and H3 (the first two sets of terms in each model) are often adequate. Snee (1973) discussed the types of

curvature generated by these second-order Becker models over the region $0 \leq x_i \leq 1$.

Becker further noted that the forms of H1, H2, and H3 implicitly assume the response surface attains its maximum (or minimum) at the centroid of the simplex. He suggested alternate forms of the models for situations where this is not the case (see Becker 1968 or Cornell 1981).

Draper and St. John (1977a) proposed several mixture models which consist of Scheffé canonical polynomial models plus inverse terms of the form x_i^{-1}. For example, the first and second-degree models with inverse terms are

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i=1}^{q} \beta_{-i} x_i^{-1} \tag{2.9}$$

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} x_i x_j + \sum_{i=1}^{q} \beta_{-i} x_i^{-1} \; . \tag{2.10}$$

Inverse terms may be added to any Scheffé polynomial model in a similar manner.

An inverse term x_i^{-1} proves helpful in situations where an extreme change in the response ($f(\underline{x}) \to \pm\infty$) occurs as the proportion of a component tends to its lower bound of zero. For similar situations where a component has a non-zero lower bound L_i, inverse terms of the form $(x_i - L_i)^{-1}$ may be used. If $f(\underline{x}) \to \pm\infty$ as $x_i \to U_i$ (where U_i represents the component's upper bound such that $0 \leq L_i < U_i \leq 1$), then inverse terms of the form $(U_i - x_i)^{-1}$ are appropriate.

It is assumed when using any of the above models with inverse terms that the experimental region itself does not include the boundary of any component i that causes $f(\underline{x}) \to \pm\infty$ as $x_i \to L_i$ or U_i. See Draper and St. John (1977a) for further discussion of this assumption.

In some mixture experiments, interest centers around ratios of component proportions and how the response depends on these ratios (see e.g., Hackler, Kriegel, and Hader 1956 or Kenworthy 1963). Snee (1973) noted that models based on ratios are useful alternatives to the Scheffé and Becker models for particular types of surfaces because the ratio models describe a different type of curvature than do the other models.

A ratio model is developed by replacing the set of component proportions x_i, i=1,2, . . . ,q, with an equivalent set of ratio variables r_j, j=1,2, . . . ,q-1. In general, there are many possibilities. For example, with three components the following equivalent transformations (among others) are possible:

Transformation	r_1	r_2
R1	x_1/x_2	x_2/x_3
R2	x_1/x_2	x_3/x_2
R3	x_1	x_2/x_3
R4	$x_1/(x_2 + x_3)$	x_2/x_3

It is seen that ratios may not be defined if certain

component proportions take on zero values in the denominator. In such cases, Snee (1973) suggested adding a small positive quantity c to each x_i so that the denominator is always greater than zero.

The above example illustrates that only q-1 ratio variables are needed to replace the q component proportions (owing to the mixture restriction $\sum_{i=1}^{q} x_i = 1$). Because of this reduction in the number of variables, the ratio variables are mathematically independent. Hence, standard polynomial models in the ratio variables, such as

$$\eta = \alpha_0 + \sum_{j=1}^{q-1} \alpha_j r_j \tag{2.11}$$

and

$$\eta = \alpha_0 + \sum_{j=1}^{q-1} \alpha_j r_j + \sum_{j<k}^{q-1} \sum \alpha_{jk} r_j r_k + \sum_{j=1}^{q-1} \alpha_{jj} r_j^2 \tag{2.12}$$

may be used. Further discussion of ratio models may be found in Snee (1973) and Cornell (1981).

Becker (1978) presented additional models for mixture experiments with additive or inactive components. For q = 3, Becker suggested the following model form when at least one component is inactive:

$$\eta = \beta_0 + \beta_1 x_1/(x_1+x_2) + \beta_2 x_2/(x_2+x_3) + \beta_3 x_3/(x_3+x_1) + \sum_{i<j}^{q} \sum \beta_{ij} h_{ij}(x_i,x_j) + \beta_{123} h_{123}(x_1,x_2,x_3) . \tag{2.13}$$

Here h_{ij} and h_{123} are specified functions which are homogeneous of degree zero. Inactivity of a component x_i is suspected when $\beta_i = 0$, $\beta_{ij} = 0$ for $j \neq i$, and $\beta_{123} = 0$. The h_{ij} and h_{123} functions suggested by Becker are

$$h_{ij}(x_i,x_j) = \left(\frac{x_i}{x_i+x_j}\right)^{s_i} \left(\frac{x_j}{x_i+x_j}\right)^{s_j} \qquad (2.14)$$

$$h_{123}(x_1,x_2,x_3) = \left(\frac{x_1}{x_1+x_2}\right)^{t_1} \left(\frac{x_2}{x_2+x_3}\right)^{t_2} \left(\frac{x_3}{x_3+x_1}\right)^{t_3} . \qquad (2.15)$$

He also noted that when s_i or t_i is negative, h_{ij} or h_{123} takes on an extremely large value near the boundary $x_i = 0$. Models of the form (2.13) are then alternatives to the inverse term models of Draper and St. John (1977a) discussed earlier.

Becker (1978) also made a general model suggestion for mixture experiments with additive components, extending his earlier work (Becker 1968). This suggestion is to consider the model

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} (x_i+x_j)h_{ij}(x_i,x_j) + \ldots + \beta_{12\ldots q}(x_1+\ldots+x_q)h_{12\ldots q}(x_1,\ldots,x_q) , \qquad (2.16)$$

where the functions $h_{ij}(x_i,x_j)$, $h_{ijk}(x_i,x_j,x_k)$, etc. are homogeneous of degree zero. This model can be simplified by deleting higher order terms. Becker (1978) gave some

suggestions for the h functions, and noted that the H2 and H3 models of (2.7) and (2.8) are of the form (2.16).

Aitchison and Bacon-Shone (1984) presented the polynomial models

$$\eta = \beta_0 + \sum_{i=1}^{q-1} \beta_i z_i \tag{2.17}$$

$$\eta = \beta_0 + \sum_{i=1}^{q-1} \beta_i z_i + \sum_{i<j}^{q-1} \sum \gamma_{ij} z_i z_j \quad , \tag{2.18}$$

where $z_i = \log(x_i/x_q)$, $i=1,2, \ldots ,q-1$. Rewriting (2.17) and (2.18) in terms of the component proportions x_i gives the symmetric model forms

$$\eta = \beta_0 + \sum_{i=1}^{q} \beta_i \log x_i \qquad (\sum_{i=1}^{q} \beta_i = 0) \tag{2.19}$$

$$\eta = \beta_0 + \sum_{i=1}^{q} \beta_i \log x_i + \sum_{i<j}^{q} \sum \beta_{ij} (\log x_i - \log x_j)^2 \quad , \tag{2.20}$$

where the β_{ij} are functions of the γ_{ij}. Note that the above models are not directly applicable when the component proportions take on zero values, since $\log x_i \to -\infty$ as $x_i \to 0$. This behavior suggests models (2.19) and (2.20) as alternatives to the inverse term models of Draper and St. John (1977a) when the component proportions approach but do not equal zero-valued boundaries. Substituting $x_i - L_i$ or $U_i - x_i$ for x_i in (2.19) or (2.20) yields models useful for

constrained mixture experiments where $f(\underline{x}) \to \pm\infty$ as $x_i \to L_i$ or U_i.

Aitchison and Bacon-Shone pointed out that

$$\beta_i = 0 \ (i=1,\ldots,c); \ \beta_{ij} = 0 \ (1 \leq i < j \leq c) \tag{2.21}$$

indicates the inactivity of components 1, 2, . . . , c. They also noted that

$$\beta_{ij} = 0 \ (i=1,2,\ldots,c; \ j=c+1,\ldots,q) \tag{2.22}$$

indicates that components 1, 2, . . . , c are additive with respect to components c+1, c+2, . . . , q. This is a more general concept of additivity than that considered by Becker (1968, 1978), where he implied

$$\beta_{ij} = 0 \ (i=1,2,\ldots,c; \ j=i+1,\ldots,q) \tag{2.23}$$

indicates that components 1, 2, . . . , c are additive.

2.2 Mixture Experiment Designs

As with any response surface problem, choosing an experimental design is an important part of a mixture experiment. Designs for both constrained and unconstrained mixture experiments are reviewed.

Scheffé (1958) proposed the {q,m} simplex-lattice designs for exploring the full q-component simplex region in an unconstrained mixture experiment. The {q,m}

simplex-lattice design (m=1,2, . . .) consists of the $\binom{q+m-1}{m}$ points in the simplex (1.11) that represent all possible mixtures obtainable when the proportion of each component can take on the values 0, 1/m, 2/m, . . . , 1. Examples of some {q,m} simplex-lattices are given in Figure 2.1.

The simplex-lattice gives an equally spaced distribution of points over the simplex (1.11) and enables a Scheffé canonical polynomial of degree m in the x_i to be fitted exactly. For example, a {q,2} simplex-lattice supports the fitting of the Scheffé canonical polynomial model (2.4), while a {q,3} simplex-lattice supports the fitting of model (2.5).

Scheffé (1963) presented the simplex-centroid designs and associated "special" canonical polynomial models for unconstrained mixture experiments. The simplex-centroid design consists of $2^q - 1$ points: the q pure components, the $\binom{q}{2}$ two-component blends with equal proportions of 1/2 for each of the proportions present, the $\binom{q}{3}$ three-component blends with equal proportions of 1/3 for each of the components present, . . . , and the q-component blend with equal proportions of 1/q for all components. The simplex-centroid design contains blends involving every subset of the q components where the components present in any blend occur in equal proportions. Examples are given in Figure 2.2.

The simplex-centroid design has an associated "special" canonical polynomial model

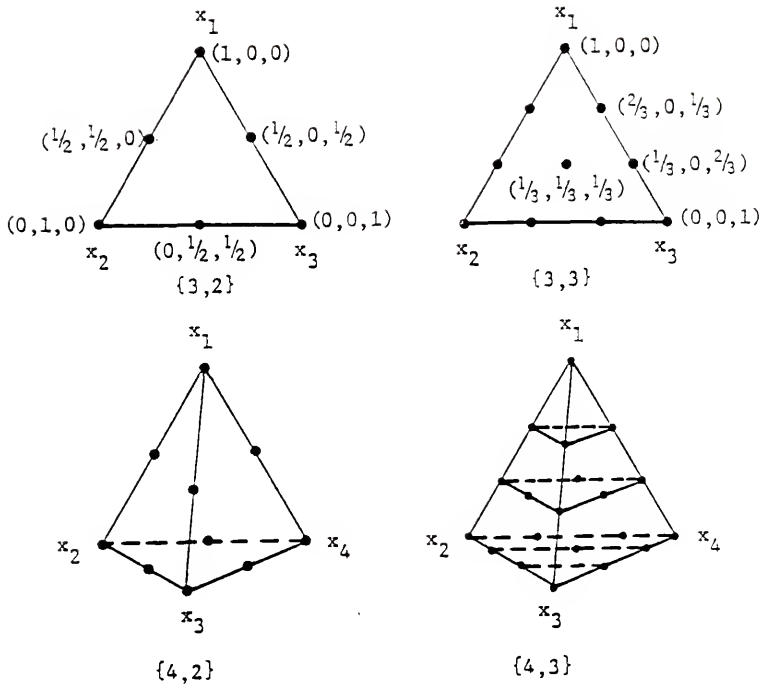


Figure 2.1 Some {q,m} Simplex-Lattice Designs for Three and Four Components

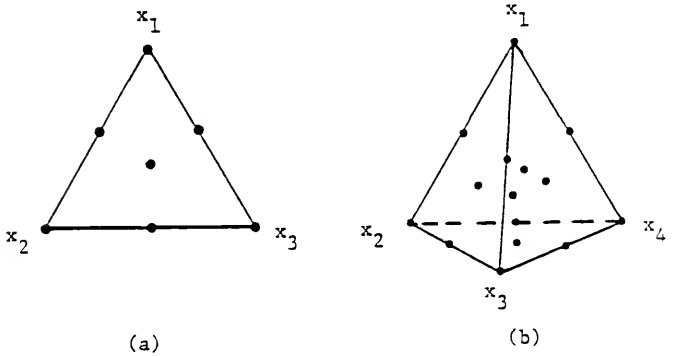


Figure 2.2 Simplex-Centroid Designs for (a) Three Components and (b) Four Components

$$\eta = \sum_{i=1}^{q} \beta_i x_i + \sum_{i<j}^{q} \sum \beta_{ij} x_i x_j + \sum_{i<j<k}^{q} \sum \beta_{ijk} x_i x_j x_k$$

$$+ \cdots + \beta_{12\ldots q} x_1 x_2 \cdots x_q \,. \qquad (2.24)$$

This model contains $2^q - 1$ terms and hence provides an exact fit to data collected at the points of the corresponding simplex-centroid design. The special-cubic model

$$\eta = \sum_{i=1}^{3} \beta_i x_i + \sum_{i<j}^{3} \sum \beta_{ij} x_i x_j + \beta_{123} x_1 x_2 x_3 \qquad (2.25)$$

is an example of (2.24) for the case $q = 3$.

Becker (1978) proposed <u>radial designs</u> for mixture experiments for the purpose of detecting inactive components or components with additive effects. He defined a radial design as one in which all points lie on straight lines (rays) extending from one or more focal points. For unconstrained mixture experiments, focal points of interest are the vertices of the simplex ($x_i = 1$, $x_j = 0$, $j \neq i$) corresponding to those components thought to have additive effects or thought to be inactive components. For constrained mixture problems, focal points might be the simplex vertices, the vertices of the pseudocomponent simplex, or other points depending on how the concept of a component effect is to be defined (see Piepel 1982).

The radial designs of Becker (1978) are an extension of the <u>axial designs</u> proposed by Cornell (1975). The axis of

component i is the imaginary line extending from the vertex $x_i = 1$, $x_j = 0$, $j \neq i$, to the point $x_i = 0$, $x_j = 1/(q-1)$, $j \neq i$, on the opposite boundary. The points of an axial design lie only on the component axes. Cornell and Gorman (1978) illustrated the use of an axial design for detecting an additive blending component. Other uses for axial designs have been discussed by Cornell (1975, 1977).

Draper and St. John (1977b) presented D_N-optimal designs corresponding to their mixture models with inverse terms (2.9) and (2.10), for three and four components. The points of support upon which the D_N-optimal designs for models (2.9) and (2.10) with three components are based, are shown in Figure 2.3. For the designs displayed in Figure 2.3, it was assumed that $x_i \geq 0.05$, i=1,2,3 to avoid the problems that occur in x_i^{-1} when $x_i = 0$.

Standard response surface designs such as factorials and central composite designs are appropriate for fitting polynomial models in ratio variables. Kenworthy (1963) discussed factorial designs for situations where each ratio variable is of the form $r_k = x_i/x_j$. Hackler, Kriegel, and Hader (1956), Donelson and Wilson (1960), Kissell and Marshall (1962), and Kissell (1967) all used central composite designs in situations where their ratio variables were defined using ratio functions of the form $r_i = x_i/(x_i+x_j+ \ldots)$.

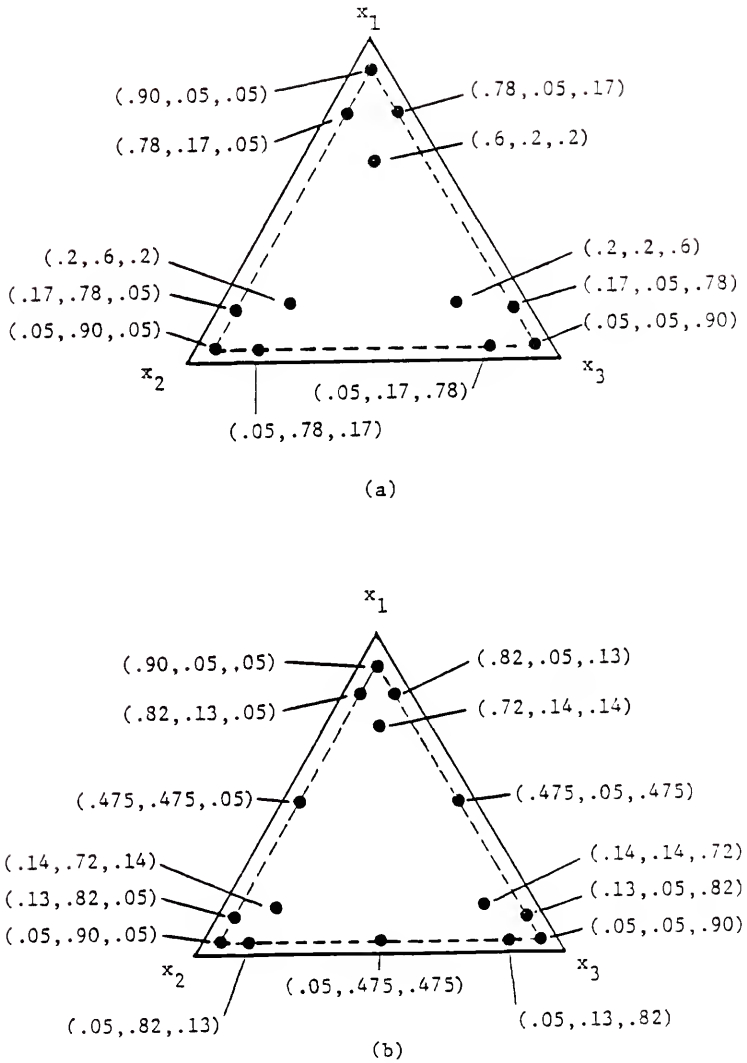


Figure 2.3. Points of Support of D_N-Optimal Designs for Models 2.9 (a) and 2.10 (b)

Aitchison and Bacon-Shone (1984) did not discuss designs for their log-ratio models. However, it is clear from the polynomial forms (2.17) and (2.18) that standard response surface designs (such as factorials and central composite designs) in the $z_i = \log(x_i/x_j)$ are applicable.

Most of the designs discussed above were originally proposed for unconstrained mixture experiments. For certain constrained mixture experiments where the constraint region is again a regular simplex, the designs discussed so far can be adapted by using a pseudocomponent transformation. However, most constrained mixture experiments have an irregular hyperpolyhedron as a constraint region. We now discuss designs for this type of constrained mixture experiment.

McLean and Anderson (1966) presented an algorithm for generating the vertices of the constraint region given the lower (L_i) and upper (U_i) bounds for the component proportions. For fitting the Scheffé second-degree canonical polynomial model (2.4), they suggested using the vertices and face centroids of the constraint region, and referred to such designs as extreme vertices designs.

Snee and Marquardt (1974) presented an algorithm called XVERT, for generating vertices of a constraint region. Additionally, the XVERT algorithm helps one choose an efficient experimental design for fitting the first-degree canonical polynomial model (2.3), by selecting only a subset

of all extreme vertices. The approach of Snee and Marquardt includes the use of the D_N, G_N, and A_N-optimality criteria in choosing efficient designs.

Nigam, Gupta, and Gupta (1983) presented the XVERT1 algorithm for generating designs for fitting the first-degree canonical polynomial model (2.3). The XVERT1 algorithm is considerably faster than XVERT since it does not depend on any of the optimality criteria (D_N, G_N, V_N, and A_N-optimality) in building a design. Resulting designs compare well with those developed by XVERT with respect to measures such as G-efficiency, $\det(X'X)$, and $\mathrm{tr}[(X'X)^{-1}]$.

Snee (1975) discussed the development of mixture designs for fitting the second-degree canonical polynomial model (2.4) in constrained regions. For $3 \leq q \leq 5$, Snee suggested the design should consist of the vertices, all constraint plane centroids, the overall centroid, and the centroids of long edges. For $q \geq 5$, Snee suggested using a computer-aided design approach to select design points from a list of candidates comprised of the vertices, edge centroids, face centroids, and overall centroid.

Goel (1980) discussed the UNIEXP algorithm which assigns points uniformly over the constraint region. Goel claimed that designs generated with the UNIEXP algorithm compare favorably with those developed by the computer-aided design approach of Snee (1975).

Saxena and Nigam (1977) presented a transformational approach for adapting the symmetric simplex designs of Murty and Das (1968) to constrained mixture experiments. Murthy and Murty (1983) discussed a transformational approach for adapting factorial (fractional or complete) designs for constrained mixture experiments. Both approaches differ from the approach of Snee (1975) in that some points are placed inside the region, whereas Snee's design points are placed primarily on the constraint region boundaries.

2.3 Mixture-Process Variable Experiments

In mixture experimentation, it may be of interest to observe changes in the response values caused by varying the levels of n process variables in addition to the q mixture component proportions. Scheffé (1963) gave an example where the response is "road octane number" of a blend of gasolines, and the make and speed of the car might be varied as well as the proportions of the gasolines.

Since the main purpose of Scheffé's article was to introduce the simplex-centroid design, he naturally suggested a simplex-centroid x (k_1 x k_2 x . . . x k_n) factorial arrangement for mixture-process variable experiments (where k_j represents the number of levels of the jth process variable). Such an arrangement can be thought of as a simplex-centroid design at each of the k_1 x k_2 x . . . x k_n factorial points or alternately as an (k_1 x k_2 x

. . . x k_n) factorial at each of the $2^q - 1$ simplex-centroid points.

Scheffé also discussed an associated model for the simplex-centroid x (k_1 x k_2 x . . . x k_n) design. The notation gets rather messy if the process variables are considered as classification variables, and there are more than two levels of each factor. For process variables z_1, z_2, . . . , z_n measured on a continuous scale, the model can be represented somewhat easier. As an illustration, the model for q = 3 components and n = 2 process variables, where each process variable is set at two levels, is given by

$$\begin{aligned} \eta = {} & \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_3^0 x_3 + \beta_{12}^0 x_1 x_2 + \beta_{13}^0 x_1 x_3 + \beta_{23}^0 x_2 x_3 \\ & + \beta_{123}^0 x_1 x_2 x_3 + \sum_{j=1}^{2} [\beta_1^j x_1 + \beta_2^j x_2 + \ldots + \beta_{23}^j x_2 x_3 \\ & + \beta_{123}^j x_1 x_2 x_3] z_j + [\beta_1^{12} x_1 + \beta_2^{12} x_2 + \ldots + \beta_{23}^{12} x_2 x_3 \\ & + \beta_{123}^{12} x_1 x_2 x_3] z_1 z_2 \cdot \end{aligned} \tag{2.26}$$

In general, when there are n process variables each at two levels, the complete canonical polynomial contains $2^{q+n} - 2^n$ terms and is of degree q+n in the x's and z's.

Note in (2.26) that there are no terms involving only the process variables (main effects of the process variables

or interactions containing only process variables). This is due to the identity $x_1 + x_2 + \ldots + x_q = 1$.

The number of points in the simplex-centroid x factorial design increases rapidly with the number of mixture and process variables q and n. Scheffé (1963) discussed two fractionation methods for reducing the number of points in a simplex-centroid x 2^n design. The first method is somewhat complicated and will not be discussed here. The second fractionation method sets up a 1:1 correspondence between the $(2^q - 1)2^n$ points of the simplex-centroid x 2^n design and the points of a 2^{q+n} design (after removing the 2^n points corresponding to those combinations where all of the q mixture components are absent). A fraction of the simplex-centroid x 2^n design is obtained by taking the points corresponding to those in a fraction of the 2^{q+n} design. Points in the resulting design that have one mixture component present correspond to pure mixtures, points with two mixture components present correspond to binary mixtures with each component proportion equaling 1/2, . . . , and so on. The process variable combinations of high and low levels of the z_i at these mixture points are interpreted as usual. As an example, for q = 5 and n = 2 let A, B, C, D, and E represent the mixture components and let F and G represent the two process variables. Then the point "acdg" in the 2^7 design is the mixture composition

(1/3,0,1/3,1/3,0) run at the low level of process variable F and at the high level of process variable G.

Cornell and Gorman (1984) presented various fractional design plans for mixture-process variable experiments with $q = 2$ or 3 components and with $n = 3$ process variables each at two levels. They utilized Scheffé's second fractionation method and considered designs for fitting mixture-process variable models containing fewer than the $2^{q+n} - 2^n$ terms in the complete model.

It was noted earlier that there are no terms in Scheffé's mixture-process variable models [e.g. (2.26)] involving only the process variables. Gorman and Cornell (1982) discussed reparametrized model forms that do contain such terms. They introduced a simple example to illustrate their work. For a two-component mixture experiment with one process variable (at two levels), they considered the canonical polynomial model

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2 + (\beta_1^1 x_1 + \beta_2^1 x_2 + \beta_{12}^1 x_1 x_2) z_1 . \qquad (2.27)$$

The effects of the process variable z_1 are contained in the coefficients β_1^1, β_2^1, and β_{12}^1. If z_1 has the same (constant) effect on all compositions, then $\beta_1^1 = \beta_2^1$ and $\beta_{12}^1 = 0$, yielding the reduced model

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2 + \beta_0^1 z_1 \ , \qquad (2.28)$$

where $\beta_0^1 = \beta_1^1 = \beta_2^1$. Note that the terms in (2.28) are not a subset of the terms in (2.27), specifically $\beta_0^1 z_1$ is not contained in (2.27). Gorman and Cornell also noted that one can get a distorted view of the effects and significance of z_1 by considering (2.27).

To arrive at a reduced form of the combined model in the x_i's and z_i's, Gorman and Cornell suggested reparametrizing the general form of the mixture-process variable canonical polynomial model by first substituting $1 - \sum_{j=2}^{q} x_j$ for x_1 in all crossproduct terms involving x_1 (alone) with the process variables and then rewriting the terms in the model. For the above example, substituting $1 - x_2$ for x_1 in the term $\beta_1^1 x_1 z_1$ in (2.27) yields

$$\begin{aligned}\eta &= \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2 + \beta_1^1 (1 - x_2) z_1 \\ &\quad + \beta_2^1 x_2 z_1 + \beta_{12}^1 x_1 x_2 z_1 \\ &= \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2 + \delta_2^1 x_2 z_1 \\ &\quad + \beta_{12}^1 x_1 x_2 z_1 + \beta_0^1 z_1 \ , \end{aligned} \qquad (2.29)$$

where $\delta_2^1 = \beta_2^1 - \beta_1^1$ and $\beta_0^1 = \beta_1^1$. Hence, δ_2^1 represents the difference between the effect of z_1 on the linear blending of x_2 and x_1 while β_0^1 represents the effect of z_1 on the

linear blending of x_1. Note that when the terms $\delta_2^1 x_2 z_1$ and $\beta_{12}^1 x_1 x_2 z_1$ are omitted from (2.29), we obtain (2.28). Hence, the reparametrized model is suitable for obtaining reduced model forms through subset selection procedures. Also, note that the reparametrized form (2.29) now has a term with z_1 alone. But, as noted above, the coefficient β_0^1 of z_1 represents the effect of z_1 on the linear blending of x_1, not an overall main effect of z_1 (unless both δ_2^1 and β_{12}^1 are zero, in which case β_0^1 is a measure of the overall main effect of z_1).

In closing this section, it should be noted that Scheffé's mixture-process variable models are still applicable for constrained mixture-process variable experiments. The concept of a mixture x factorial design (and a fraction thereof) is valid and can be used in situations where the mixture design is defined for studying the response surface over a constrained region.

CHAPTER THREE
MODELS FOR MIXTURE-AMOUNT EXPERIMENTS

In the usual definition of a mixture experiment (Cornell 1981, Scheffé 1958), the response is said to depend only on the proportions of the components present in the mixture and not on the total amount of the mixture. This definition has often prompted the question, "If the total amount of the mixture also affects the response, do we still have a mixture experiment?" Based on the above definition, the answer is no. However, a mixture experiment in which the amount of the mixture varies and affects the response is a general mixture experiment (as defined in Section 1.3).

3.1 An Introduction to Mixture-Amount Experiments

A general mixture experiment in which a (usual) mixture experiment is conducted at each of several total amounts will be referred to as a mixture-amount experiment. An example of a mixture-amount experiment is the application of fertilizer, where the amount (level) of fertilizer applied is allowed to vary and the different levels can affect the yield as much as the fertilizer formulation. Another example is the treatment of a disease with drugs, where both

the amount and composition of the drug affect the speed and quality of recovery that occurs.

This generalization of the definition raises many questions about the design, modeling, and analysis of mixture-amount experiments. For example:

1. Are the blending properties of the mixture components affected by varying the total amount of the mixture? If so, how?
2. If the blending properties of the component are not affected by the total amount, what effect if any does varying the total amount have on the response?
3. What model forms are appropriate for measuring the component blending properties and the total amount effects mentioned in questions 1 and 2 above?
4. What type of designs should be used to develop models to answer the above questions?
5. Finally, if there are process variables in the mixture experiment, how are their effects affected, if at all, by varying the total amount of the mixture?

In this chapter, models and designs that relate to questions 1, 2, 3, and 4 are discussed. Mixture-amount experiments with process variables are discussed briefly in Appendix G.

Before proceeding with model development, several simple hypothetical situations are presented to illustrate what is meant in the first two questions above by the total amount affecting the component blending properties. Consider a mixture-amount experiment with $q = 2$ components and a total amount variable A at two levels (say $A_1 < A_2$). Suppose the two components blend linearly at both amounts.

Several possible situations are shown in Figure 3.1, where the pure component proportions are denoted by (x_1,x_2) = (1,0) and (0,1). Figure 3.1(a) illustrates the case where changing the level of the total amount has no effect on the response (the lines are coincident), while in Figure 3.1(b) increasing the amount from A_1 to A_2 increases the response at all mixtures by a constant amount. Note that Figure 3.1(b) illustrates a situation where the total amount does not affect the component blending properties but does affect the response. Figures 3.1(c) and (d) illustrate cases where the total amount does affect the component blending properties. In Figure 3.1(c), we see that an increase in the value of the response results from raising the level of the amount of the mixture, and the effect of raising the amount becomes larger as the proportion of component 2 in the mixture increases. Figure 3.1(d) represents a situation where changing the amount has a considerable effect on the blending properties of the two components; at A_1, increasing the proportion x_2 produces an increase in the response value, while at A_2 it results in a decrease in the response value.

3.2 Including the Total Amount in Mixture Models

Since the response in a typical mixture experiment does not depend on the total amount, the usual mixture model forms must be modified to incorporate amount effects for

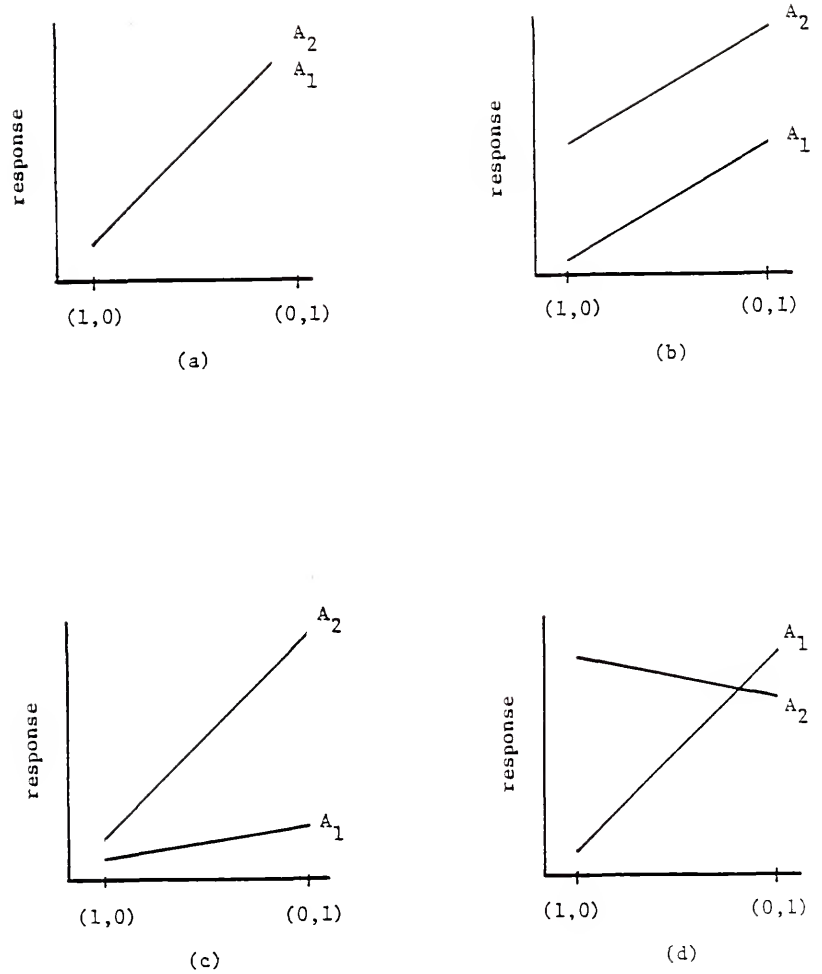


Figure 3.1. Plots of Several Two-Component Blending Systems at Two Total Amounts A_1 and A_2

fitting data from a mixture-amount experiment. A technique for doing so is suggested by recognizing the similarity of a mixture-amount experiment to a mixture experiment with one process variable. Likewise, a mixture-amount experiment with n process variables is similar to a mixture experiment with n+1 process variables.

Scheffé (1963) developed models for mixture experiments with process variables by considering the parameters of his canonical polynomial mixture models as being dependent on the process variable effects (these models were presented in Section 2.3). This same technique can be adapted for mixture-amount experiments with or without process variables. Mixture-amount experiments without process variables are discussed in this chapter. The extension to mixture-amount experiments with process variables is discussed in Appendix G.

3.3 Mixture-Amount Models Based on Scheffé Canonical Polynomials

Scheffé's canonical polynomials (see Section 2.1) have been shown to be a versatile class of equations for modeling mixture response surfaces. Since a mixture-amount experiment is just a series of mixture experiments run at each of several amounts $A_1, A_2, \ldots, A_r$, $r \geq 2$, it is natural to envision fitting the entire experimental data set as a series of smaller experiments which are performed at each

amount A_i. We consider the fitting of a Scheffé canonical polynomial model such as (2.3) or (2.4) at each amount.

To begin the development, suppose a particular Scheffé canonical polynomial model form, denoted by η_C, adequately describes the component blending at each of the r levels of A. If the total amount of the mixture affects the response, the parameters of η_C vary as A varies, i.e., the parameters of η_C depend on A. This dependence can be modeled (for each parameter β_m in η_C) using the standard polynomial form

$$\beta_m(A) = \beta_m^0 + \sum_{k=1}^{r-1} \beta_m^k (A')^k \ , \tag{3.1}$$

where $\beta_m(A)$ denotes that the parameter is considered to be a function of A, and A' denotes a coded version of A. Although (3.1) implies an (r-1)th degree polynomial can be used if desired, a second-degree polynomial will often suffice in practice. Nonpolynomial functions of A that might also be appropriate for certain applications are

$$\beta_m(A) = \beta_m^0 + \sum_{k=1}^{r-1} \beta_m^k A^{-k} \tag{3.2}$$

or

$$\beta_m(A) = \beta_m^0 + \sum_{k=1}^{r-1} \beta_m^k (\log A)^k \ . \tag{3.3}$$

In practice, A^{-1} and log A in the above equations would usually be coded, as was A in (3.1).

By writing the parameters in a Scheffé canonical polynomial model as functions of A, a new model is obtained that enables us to measure the effects of total amount on the blending properties of the components. This model derivation technique may be applied to any of the mixture models reviewed in Section 2.1 (see Section 3.4). Any model obtained in this manner will be referred to as a mixture-amount model.

As an example, let us derive the form of a quadratic by quadratic mixture-amount model where q = 2 and r = 3. Then, η_C is of the form (2.4) and the β_m's are of the form (3.1), which yields

$$\begin{aligned}\eta &= \beta_1(A)x_1 + \beta_2(A)x_2 + \beta_{12}(A)x_1x_2 \\ &= [\beta_1^0 + \beta_1^1 A' + \beta_1^2(A')^2]x_1 + [\beta_2^0 + \beta_2^1 A' + \beta_2^2(A')^2]x_2 \\ &\quad + [\beta_{12}^0 + \beta_{12}^1 A' + \beta_{12}^2(A')^2]x_1x_2 \\ &= \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1x_2 \\ &\quad + \sum_{k=1}^{2} [\beta_1^k x_1 + \beta_2^k x_2 + \beta_{12}^k x_1x_2](A')^k . \end{aligned} \tag{3.4}$$

Note that the subscript of a β parameter in (3.4) refers to the components that are present in the associated term while the superscript refers to the power of the A' variable for that term.

When the levels A_1, A_2, A_3 are coded to have zero mean (usually -1, 0, +1 if the levels are equally spaced), the terms in the combined model (3.4) have the following interpretation:

i) $\beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2$ represents the linear and nonlinear blending properties of the mixture components at the average level of total amount,

ii) $[\beta_1^1 x_1 + \beta_2^1 x_2 + \beta_{12}^1 x_1 x_2]A'$ represents the linear effect of total amount on the linear and nonlinear blending properties of the mixture components,

iii) $[\beta_1^2 x_1 + \beta_2^2 x_2 + \beta_{12}^2 x_1 x_2](A')^2$ represents the quadratic effect of total amount on the linear and nonlinear blending properties of the mixture components.

Thus the coefficients β_i^k and β_{ij}^k of the terms $x_i(A')^k$ and $x_i x_j(A')^k$, k=1,2, in (3.4) are measures of the effects of changing the amount of the mixture on the linear and nonlinear blending properties of the mixture components (at the average level of total amount).

When the levels of A' and $(A')^2$ are coded to be the coefficients of orthogonal polynomials [i.e., when A' and $(A')^2$ in (3.4) are replaced by the first and second-degree orthogonal polynomials $P_1(A)$ and $P_2(A)$], the interpretations of the coefficients change somewhat. Under this coding, the

coefficients β_1^0, β_2^0, and β_{12}^0 measure the linear and nonlinear blending properties of the components averaged over the levels of total amount. The coefficients β_i^k and β_{ij}^k, k=1,2, are measures of the effects of changing the amount of the mixture on the linear and nonlinear blending properties of the mixture components (averaged over the levels of total amount). See Section B.2 of Appendix B for an example that illustrates the above interpretations.

For general q and r, a model of the form (3.4) is written as

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{k=1}^{r-1} \left[\sum_{i=1}^{q} \beta_i^k x_i + \sum_{i<j}^{q} \beta_{ij}^k x_i x_j \right] (A')^k . \qquad (3.5)$$

Depending on the way in which changing the total amount affects the component blending for a particular application, all of the terms in (3.5) may or may not be needed. Several reduced forms of (3.5) that may be appropriate for various applications are listed and discussed in Appendix A.

Suppose now the amount of the mixture does not affect the blending properties of the components but does have an effect on the value of the response. For the model of (3.5), this implies that A has a constant linear effect for all compositions (which forces $\beta_1^1 = \beta_2^1 = \ldots = \beta_q^1$ and $\beta_{12}^1 = \beta_{13}^1 = \ldots = \beta_{q-1,q}^1 = 0$); that A has a constant quadratic

effect for all compositions (which forces $\beta_1^2 = \beta_2^2 = \ldots = \beta_q^2$ and $\beta_{12}^2 = \beta_{13}^2 = \ldots = \beta_{q-1,q}^2 = 0$); . . . ; and that A has a constant (r-1)th degree effect for all compositions (which forces $\beta_1^{r-1} = \beta_2^{r-1} = \ldots = \beta_q^{r-1}$ and $\beta_{12}^{r-1} = \beta_{13}^{r-1} = \ldots = \beta_{q-1,q}^{r-1} = 0$). In this case, the model of (3.5) takes the reduced form

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{k=1}^{r-1} \beta_0^k (A')^k , \qquad (3.6)$$

where the β_0^k ($= \beta_1^k = \ldots = \beta_q^k$), k=1,2, . . . ,r-1, represent the linear, quadratic, . . . , (r-1)th degree effects of total amount on the response. Several reduced forms of (3.6) that are of the most practical interest are also presented and discussed in Appendix A.

Note that the terms of (3.6) are not a subset of the terms of (3.5); specifically the terms with A' alone ($\beta_0^k (A')^k$, k=1,2, . . . ,r-1) are not contained in (3.5). This means that a subset regression procedure cannot be used on (3.5) to arrive at the form (3.6). This problem may be alleviated by reparametrizing (3.5) as suggested by Gorman and Cornell (1982). The reparametrization involves replacing x_q with $1 - \sum_{i=1}^{q-1} x_i$ in the terms $\beta_q^k x_q (A')^k$, k=1,2, . . . ,r-1, of (3.5) and simplifying. For the q = 2, r = 3 example considered earlier (3.4) is reparametrized as

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2$$

$$+ \sum_{k=1}^{2} [\beta_1^k x_1 + \beta_2^k (1 - x_1) + \beta_{12}^k x_1 x_2](A')^k$$

$$= \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1 x_2$$

$$+ \sum_{k=1}^{2} [\delta_2^k x_1 + \beta_{12}^k x_1 x_2 + \beta_0^k](A')^k , \qquad (3.7)$$

where $\delta_2^k = \beta_1^k - \beta_2^k$ and $\beta_0^k = \beta_2^k$, k=1,2. Hence, δ_2^1 represents the difference between the linear effects of total amount on the linear blending properties of x_1 and x_2, and δ_2^2 represents the difference between the quadratic effects of total amount on the linear blending properties of x_1 and x_2. Although (3.7) now contains the terms $\beta_0^1 A'$ and $\beta_0^2 (A')^2$ with A' and $(A')^2$ alone, note that β_0^1 (= β_2^1) and β_0^2 (= β_2^2) measure the linear and quadratic effects of total amount, respectively, on the linear blending of x_2, and do not measure the overall linear and quadratic effects of total amount [unless we find that $\delta_2^1 = \delta_2^2 = 0$ and $\beta_{12}^1 = \beta_{12}^2 = 0$ in (3.7)].

The Scheffé canonical polynomial mixture-amount models considered thus far were all developed under the assumption that the same canonical polynomial form is appropriate for describing the component blending at each total amount. Situations where the appropriate forms of the canonical polynomials at each level of total amount are different are

also of interest. Mixture-amount model forms for these situations will now be discussed.

Let us suppose one of the Scheffé canonical polynomial forms (linear, quadratic, cubic, etc.) is appropriate for describing component blending at each level of A, and that the appropriate forms are not the same for all levels of A. Further, consider the most complicated form (i.e., highest degree) that is needed at one of the levels of A. Then, if the form of the mixture-amount model is derived using this "most complicated" canonical polynomial, it will be an adequate (but overparametrized) form for fitting data from the mixture-amount experiment. The appropriate mixture-amount model form is a reduced form of the "adequate" mixture-amount model. The nature of these model reductions are determined for several situations in Appendix B.

Several canonical polynomial mixture-amount models of practical interest have been discussed in this section and are also discussed in Appendices A and B. To determine if one model is better than another, or if one model is most appropriate for a particular application, one can perform a series of full vs. reduced model tests,

$$F^* = \frac{(SSE_{reduced} - SSE_{full})/(e_r - e_f)}{SSE_{full}/e_f} , \qquad (3.8)$$

where $SSE_{reduced}$, SSE_{full}, e_r and e_f are the sum of squares for error and the error degrees of freedom for the reduced

and full models, respectively. As an example, suppose in a mixture-amount experiment that the component blending is nonlinear (quadratic), and that the total amount has at most a linear effect on the component blending properties. For this situation, we might consider the models

$$\text{Model 1:} \quad \eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \beta_0^1 A'$$

$$\text{Model 2:} \quad \eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A'$$

$$\text{Model 3:} \quad \eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \beta_{ij}^1 x_i x_j A' ,$$

which are models (A6), (A7), and (A8) in Appendix A. We begin by fitting models 3 and 2, treating them as the "full" and "reduced" models respectively, and performing the test (3.8). The test is a measure of the significance of the $q(q-1)/2$ terms $\beta_{ij}^1 x_i x_j A'$, $1 \le i < j \le q$, in model 3 over and above the contribution of the terms contained in model 2. The error degrees of freedom are $e_f = N-q(q+1)$ and $e_r = N-q(q+3)/2$, respectively. If the test is significant, model 3 is selected. If the test is not significant, then models 2 and 1 are compared, treating them as "full" and "reduced," respectively. The full vs. reduced model test (3.8) can

also be used to compare the models discussed in Appendix B to the corresponding models without parameter restrictions.

Another model selection approach is to fit the reparametrized form of a "full" mixture-amount model (such as model 3 in the above example) and use variable selection techniques such as all-possible-subsets regression or stepwise regression to determine the most appropriate model. However, the reduced models of Appendix B are not obtainable using this approach.

3.4 Mixture-Amount Models Based on Other Mixture Model Forms

In the previous section, mixture-amount models were developed by writing the parameters of Scheffé canonical polynomial models as functions of the total amount A. This technique may also be used with any of the other mixture models taken from the literature, many of which were presented in Section 2.1. Expressions such as (3.1), (3.2), (3.3) or any other appropriate function of A may be used for the parameters of the mixture model chosen. Any such model obtained by this technique is referred to as a mixture-amount model.

As an example, assume the inverse term model (2.9) is appropriate at each of two amounts, A_1 and A_2. Using β_m's of the form (3.1) yields the mixture-amount model

$$\eta = \sum_{i=1}^{q} \beta_i(A)x_i + \sum_{i=1}^{q} \beta_{-i}(A)x_i^{-1}$$

$$= \sum_{i=1}^{q} (\beta_i^0 + \beta_i^1 A')x_i + \sum_{i=1}^{q} (\beta_{-i}^0 + \beta_{-i}^1 A')x_i^{-1}$$

$$= \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_{-i}^0 x_i^{-1}$$

$$+ \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i=1}^{q} \beta_{-i}^1 x_i^{-1} A' \quad . \qquad (3.9)$$

Recall that A' denotes a coded form of the total amount variable A. When the levels A_1 and A_2 are coded to have mean zero, the terms in (3.9) have the following interpretations:

(i) $\sum_{i=1}^{q} \beta_i^0 x_i$ and $\sum_{i=1}^{q} \beta_{-i}^0 x_i^{-1}$ respectively represent the linear and nonlinear blending properties of the mixture components at the average level of total amount,

(ii) $\sum_{i=1}^{q} \beta_i^1 x_i A'$ and $\sum_{i=1}^{q} \beta_{-i}^1 x_i^{-1} A'$ respectively represent the linear effects of total amount on the linear and nonlinear blending properties of the components.

The phrase "nonlinear blending" in the above interpretations

refers to an extreme increase or decrease in the response value as the value of x_i approaches zero.

As another example, assume that the second-order form of Becker's H3 model (2.8) is appropriate at each of three levels of A and that total amount has a logarithmic effect on component blending properties. The appropriate mixture-amount model is given by

$$\begin{aligned}
\eta &= \sum_{i=1}^{q} \beta_i(A)x_i + \sum_{i<j}^{q}\sum \beta_{ij}(A)(x_ix_j)^{1/2} \\
&= \sum_{i=1}^{q} [\beta_i^0+\beta_i^1(\log A)']x_i + \sum_{i<j}^{q}\sum [\beta_{ij}^0+\beta_{ij}^1(\log A)'](x_ix_j)^{1/2} \\
&= \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q}\sum \beta_{ij}^0(x_ix_j)^{1/2} \\
&\quad + \sum_{i=1}^{q} \beta_i^1 x_i(\log A)' + \sum_{i<j}^{q}\sum \beta_{ij}^1(x_ix_j)^{1/2}(\log A)' . \qquad (3.10)
\end{aligned}$$

The notation $(\log A)'$ above denotes a coded form of log A. When the three levels $\log A_1$, $\log A_2$, and $\log A_3$ are coded to have mean zero, the terms in (3.10) have the following interpretations:

(i) $\sum_{i=1}^{q} \beta_i^0 x_i$ and $\sum_{i<j}^{q}\sum \beta_{ij}^0(x_ix_j)^{1/2}$ respectively represent the linear and nonlinear blending properties of the mixture components at the average level of log (total amount),

(ii) $\sum_{i=1}^{q} \beta_i^1 x_i (\log A)'$ and $\sum_{i<j}^{q} \beta_{ij}^1 (x_i x_j)^{1/2} (\log A)'$ respectively represent the logarithmic effects of total amount on the linear and nonlinear blending properties of the mixture components.

All of the techniques discussed in Section 3.3., Appendix A, and Appendix B for deriving or reducing the Scheffé canonical polynomial mixture-amount models are applicable for any of the other types of mixture-amount models. The example models (3.9) and (3.10) will be used to illustrate this point.

Models such as (3.9) and (3.10) are appropriate for situations where the total amount affects the linear and nonlinear component blending properties similarly [e.g., in (3.9) it is assumed that the total amount has a linear effect on both the linear and nonlinear blending properties]. For situations where this is not the case, reduced models (similar to those presented in Appendix A for Scheffé canonical mixture-amount models) may be needed. For example, the reduced form of (3.9),

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_{-i}^0 x_i^{-1} + \sum_{i=1}^{q} \beta_i^1 x_i A' \quad , \tag{3.11}$$

is appropriate if the total amount has a linear effect on

the linear component blending properties but does not affect the nonlinear blending properties.

If the total amount does not affect the blending properties but does affect the response, the appropriate models for the two examples are

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_{-i}^0 x_i^{-1} + \beta_0^1 A' \qquad (3.12)$$

and

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 (x_i x_j)^{1/2} + \beta_0^1 (\log A)' \ . \qquad (3.13)$$

These models are reduced forms of (3.9) and (3.10), respectively. However, the terms in (3.12) and (3.13) are not subsets of the terms in (3.9) and (3.10). The Gorman and Cornell (1982) reparametrization technique [reexpressing x_q as $1 - \sum_{i=1}^{q-1} x_i$ in the terms $\beta_q^1 x_q A'$ of (3.9) and $\beta_q^1 x_q (\log A)'$ of (3.10)] discussed in Section 3.3 is applicable here.

For each of (3.9) and (3.10), it is implicitly assumed that the same mixture model is valid at each level of A. For situations where this is not the case, the appropriate parameter restrictions can be obtained as was done for the Scheffé canonical polynomial mixture-amount models in Appendix B. As an illustration, consider the situation specified by the mixture models

$$\eta_{A'=-1} = ax_1 + bx_2$$

$$\eta_{A'=+1} = cx_1 + dx_2 + ex_1^{-1} , \qquad (3.14)$$

where the two levels of A are coded as -1 and +1 (A' denotes the coded version of the total amount variable A). The appropriate mixture-amount model for this situation is of the form

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{-1}^0 x_1^{-1} + \beta_1^1 x_1 A' + \beta_2^1 x_2 A' + \beta_{-1}^1 x_1^{-1} A' \qquad (3.15)$$

with as yet unknown parameter restrictions. Substituting the data

x_1	x_2	A'	η
1	0	-1	a
.05	.95	-1	.05a + .95b
.50	.50	-1	.50a + .50b
1	0	1	c + e
.05	.95	1	.05c + .95d + 20e
.50	.50	1	.50c + .50d +2e

into (3.15) and solving the resulting system of equations yields the parameter estimates

$$\beta_1^0 = \frac{a+c}{2} \qquad \beta_2^0 = \frac{b+d}{2} \qquad \beta_{-1}^0 = \frac{e}{2}$$

$$\beta_1^1 = \frac{c-a}{2} \qquad \beta_2^1 = \frac{d-b}{2} \qquad \beta_{-1}^1 = \frac{e}{2} \ . \qquad (3.16)$$

The appropriate parameter restriction for this situation is thus seen to be $\beta^1_{-1} = \beta^0_{-1}$. If the inverse nonlinear blending occurred at the low level of A instead of the high level, the parameter restriction would be $\beta^1_{-1} = -\beta^0_{-1}$.

3.5 Mixture-Amount Models--A Summary

A mixture-amount model is developed by writing the parameters of any (usual) mixture model as functions of the total amount of the mixture. This modeling technique is very flexible in that any mixture model (e.g., a Scheffé canonical polynomial, one of Becker's models, a model with inverse terms, a ratio model, a log-ratio model, etc.) can be used, and the parameters may be written as any function of A. The simplest application of this mixture-amount modeling technique is to choose a mixture model which is assumed to be adequate at all levels of amount to be considered and assume that the parameters of this model are all expressible as a common function of A. However, the technique does not require that the mixture model appropriate at each level of amount be the same nor does it require that each parameter be expressible as the same function of A. Reduced forms of mixture-amount models obtained by this technique provide for many of these situations (see Appendices A and B).

The considerable flexibility of the mixture-amount modeling technique and the resultant vast number of models

to be considered raises questions about the practical aspects of selecting an appropriate mixture-amount model. A natural model selection approach is suggested when data from a complete (not fractional) mixture-amount experiment is available. Since a mixture-amount experiment is defined as being a series of usual mixture experiments run at each of several amounts, it is natural to first select (using the data) an appropriate mixture model separately for each amount. Often these individual models will all belong to a particular family (canonical polynomials, inverse-term models, etc.), in which case a "largest" member of the family adequate for all levels of amount could be fitted. Then graphical or weighted least squares (WLS) regression techniques can be used to investigate the form of functional dependence on A for each parameter. The information gained by selecting (fitting) an appropriate model at each level of A can then be used (as in Appendices A and/or B) to select the appropriate mixture-amount model. If only two levels of A are considered in the mixture-amount experiment, the graphical or WLS regression techniques will not be helpful in choosing the functional form of parameter dependence on A. Prior knowledge about the system may suggest a form such as (3.2) or (3.3) rather than the linear form (3.1).

If the available data are from a fractional mixture-amount experiment or are not from a mixture-amount experiment at all, the above "natural" approach to model

selection may not be appropriate. In such situations, the sequential "full vs. reduced" model procedure discussed at the end of Section 3.3 is appropriate. The Gorman and Cornell "reparametrization followed by variable selection" technique discussed in Section 3.3 may also be of help in such situations. The practical aspects of selecting a mixture-amount model will be considered further in Chapter 7 where several examples will be presented.

Finally, note that mixture-amount models in general are tools for answering the first two questions posed in Section 3.1. That is, if the blending properties of mixture components are affected by varying the total amount, then a mixture-amount model is appropriate for modeling the response. By coding the levels of A (or A^{-1}, log A, etc.) to have mean zero, mixture-amount models provide a description of the blending properties of the components at the average level of A (or A^{-1}, log A, etc.) and explain how the total amount affects these component blending properties. By using orthogonal polynomial functions of A (or A^{-1}, log A, etc.) in mixture-amount models, descriptions of the component blending properties averaged over the levels of A (or A^{-1}, log A, etc.) and how the total amount affects these properties are obtained. If the blending properties of the components are not affected by the total amount, then a reduced model is appropriate and explains how varying the amount affects the response (if at all).

CHAPTER FOUR
DESIGNS FOR MIXTURE-AMOUNT EXPERIMENTS

Designs for both unconstrained and constrained mixture-amount experiments are presented in this chapter. An unconstrained mixture-amount experiment is one in which the component proportions x_i vary between 0 and 1. A constrained mixture-amount experiment is one in which at least one component proportion is restricted by a nonzero lower bound or a nonunity upper bound, or by both.

In Section 4.1, a general approach to developing designs for mixture-amount experiments is presented and guidelines for selecting the levels of total amount to be investigated are given. Techniques for fractionating mixture-amount designs are discussed in Section 4.2.

4.1 Developing Designs for Mixture-Amount Experiments

Since a mixture-amount experiment is defined as a series of mixture experiments at several levels of total amount, it is natural to propose as mixture-amount designs those designs obtained by constructing a usual mixture design at each level of total amount. Usual mixture designs for both unconstrained and constrained mixture experiments were discussed in Section 2.2.

Defining a mixture-amount design as a series of separate mixture designs allows us some degree of flexibility in specifying an overall design, since the mixture designs set up at each level of total amount may or may not be the same. The family of mixture designs needed will depend on the family of mixture models selected as well as whether or not the component proportions are constrained. In practice, unless a great deal is known about the component blending properties and the effect total amount has on these properties, the same mixture model is usually considered at each level of total amount. Then, the same mixture design (corresponding to the mixture model under consideration) is constructed at each level of total amount. However, in situations where it is known beforehand that components blend differently at different amounts, or where additional investigation into the component blending at one amount is desired, one can choose to run different mixture designs at different total amounts. Also, fractionated designs (which we discuss in Section 4.2) can be viewed as different mixture designs at each level of total amount.

As an illustration of the design development process, consider a $q = 3$, $r = 3$ unconstrained mixture-amount experiment where the experimenter does not anticipate having additive or inactive components, nor does he expect extreme response behavior as component proportions approach zero.

Based on this knowledge, the experimenter selects the special-cubic canonical polynomial as being an appropriate model for describing component blending at each of the three levels of total amount. An appropriate mixture-amount design is then a three-component simplex-centroid mixture design set up at each of the three levels of total amount (see Figure 4.1). However, the experimenter may be curious as to whether or not the special cubic is adequate (i.e., Is it an underestimate of a full cubic surface?), but cannot afford to run a larger mixture design at each level of total amount. As an alternative, he may choose to run a {3,3} simplex-lattice design (for measuring the full cubic shape of the surface) at one of the levels of total amount, say at the middle level, while keeping the simplex-centroid designs at the high and low levels of total amount (see Figure 4.2).

As a second illustration, consider a constrained mixture-amount experiment with three components and two levels of total amount, where the component proportions are constrained by $.1 \leq x_1 \leq .4$, $.1 \leq x_2 \leq .3$, and $.35 \leq x_3 \leq .75$. An appropriate design for the special-cubic by linear mixture-amount model

$$\eta = \sum_{h=0}^{1} \left[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \beta_{ij}^h x_i x_j + \beta_{123}^h x_1 x_2 x_3 \right] (A')^h \qquad (4.1)$$

consists of the vertices, centroids of the longest edges, and the overall centroid of the constraint region at each of

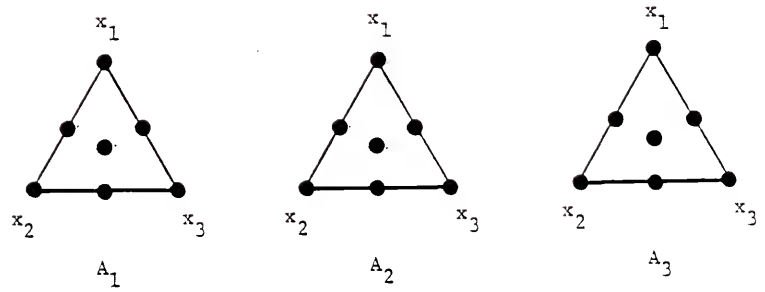


Figure 4.1. Mixture-Amount Design Consisting of a Three Component Simplex-Centroid Design at Each of Three Amounts

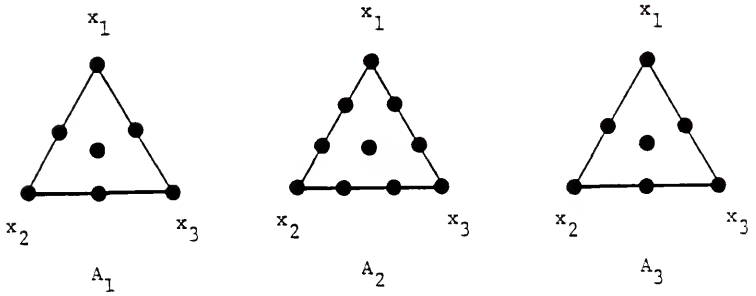


Figure 4.2. Mixture-Amount Design Consisting of a {3,3} Simplex-Lattice Design at the Middle Level and a Simplex-Centroid Design at the Low and High Levels of Total Amount

the two levels of amount (based on the recommendation of Snee 1975--see Section 2.2). The points of this design are listed in Table 4.1 and are pictured in Figure 4.3.

Another important aspect of developing designs for mixture-amount experiments is the choice of spacing for the levels of total amount. If only two levels of A are to be investigated, they should be chosen far enough apart to allow the total amount effect to be detected. However, if it is suspected that the effect of A could be quadratic but only a linear effect is desired, the two levels should be close enough so that the assumption of a linear effect of A is valid.

When a higher-than-linear effect of A is to be investigated and more than two levels of A are to be used, the choice of spacing for the levels of A will depend on what is known (or guessed) about the effect of total amount on the response. If it is believed that a polynomial function of A will adequately explain the effect of total amount, the levels of A should be equally spaced. If it is believed that a functional form such as (3.2) or (3.3) will adequately explain the effect of total amount, the levels of A should be equally spaced on a log A or A^{-1} scale, respectively. Regardless of the scale chosen, the equally spaced levels should be spread far enough apart to yield detectable differences in response as the level of A changes.

Table 4.1. Design Points for Fitting a Special-Cubic Model in a Three-Component Constrained Mixture-Amount Experiment at Two Levels of Amount

Pt[(a)]	x_1	x_2	x_3	A'
1	.10	.30	.60	-1
2	.10	.15	.75	-1
3	.15	.10	.75	-1
4	.40	.10	.50	-1
5	.40	.25	.35	-1
6	.35	.30	.35	-1
7	.225	.30	.475	-1
8	.10	.225	.675	-1
9	.275	.10	.625	-1
10	.40	.175	.425	-1
11	.25	.20	.55	-1
12	.10	.30	.60	1
13	.10	.15	.75	1
14	.15	.10	.75	1
15	.40	.10	.50	1
16	.40	.25	.35	1
17	.35	.30	.35	1
18	.225	.30	.475	1
19	.10	.225	.675	1
20	.275	.10	.625	1
21	.40	.175	.425	1
22	.25	.20	.55	1

(a) These point numbers are used in Figure 4.3.

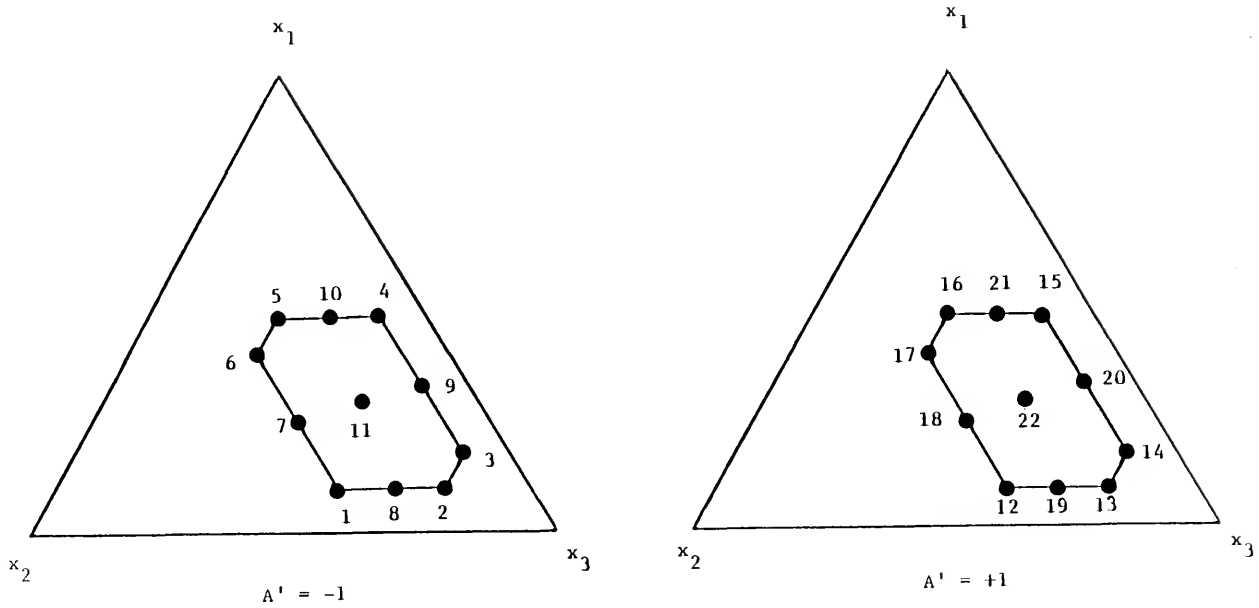


Figure 4.3. Mixture-Amount Design for Fitting a Special-Cubic Model in a Constrained Mixture-Amount Experiment

4.2 Fractionating Designs for Mixture-Amount Experiments

As q (the number of mixture components) and r (the number of levels of total amount) increase, the total number of design points in mixture-amount experiments can become excessive. The total number of design points can be reduced by running only a subset (fraction) of the points in a complete mixture-amount design. Since a reduction in the total number of design points can result in a considerable savings in terms of cost and time of experimentation, methods for fractionating mixture-amount designs are now discussed.

Fractionating mixture-amount designs is fairly straightforward for those particular situations where the overall design is a factorial design. Factorial mixture designs are appropriate for mixture models in ratio variables [e.g. (2.11) or (2.12)] or in log-ratio variables [e.g. (2.17) or (2.18)]. Running such a factorial mixture design at each of several levels of total amount yields a factorial mixture-amount design. If the q-1 mathematically independent ratio or log-ratio variables are each investigated at two levels and A is also investigated at two levels, an appropriate mixture-amount design is a $2^{q-1} \times 2 = 2^q$ factorial design. Similarly, a 3^q factorial mixture-amount design is appropriate if the q-1 ratio or log-ratio variables and the total amount variable A are each investigated at 3 levels. Fractionation methods for 2^q and

3^q designs are well known and many such fractional designs have been tabled (e.g., see Cochran and Cox 1957). Fractionation methods for the 2^k3^m series of factorial designs are discussed briefly in Appendix G with respect to mixture-amount-process variable experiments, but the techniques are applicable here also.

The second fractionation method of Scheffé (1963), discussed in Section 2.3, can be used to reduce the number of points in simplex-centroid x 2 mixture-amount designs (designs in which a q component simplex-centroid design is set up at each of two levels of total amount). In general, a simplex-centroid x 2 mixture-amount design supports fitting a mixture-amount model of the general form

$$\eta = \sum_{h=0}^{1} \Big[\sum_{i=1}^{q} \beta_i^h x_i + \sum_{i<j}^{q} \sum \beta_{ij}^h x_i x_j + \sum_{i<j<k}^{q} \sum \beta_{ijk}^h x_i x_j x_k + \cdots + \beta_{12\ldots q}^h x_1 x_2 \cdots x_q \Big] (A')^h . \qquad (4.2)$$

However, fractions of a simplex-centroid x 2 mixture-amount design will not support fitting this full model. The value of q and degree of fractionation will determine the reduced forms of (4.2) that can be fitted.

As an example, a one-half fraction of the three component simplex-centroid x 2 mixture-amount design is listed in Table 4.2 and is pictured in Figure 4.4. This seven-point design supports fitting either the special-cubic

Table 4.2. One-Half Fraction[(a)] of a Simplex-Centroid x 2 Mixture-Amount Design for Three Components

x_1	x_2	x_3	A'
1/2	1/2	0	-1
1/2	0	1/2	-1
0	1/2	1/2	-1
1	0	0	1
0	1	0	1
0	0	1	1
1/3	1/3	1/3	1

(a) Fraction obtained using I = +ABCD as the defining contrast. Switching the levels of A' yields the I = -ABCD fraction.

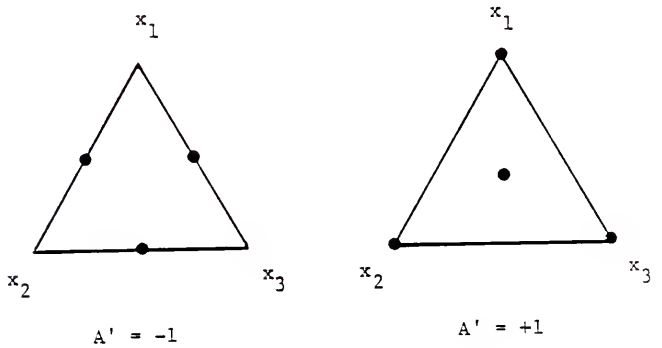


Figure 4.4. Graphical Display of Design in Table 4.2

mixture model, or, the seven-term mixture-amount model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \beta_{ij}^0 x_i x_j + \beta_0^1 A' \quad . \tag{4.3}$$

Fitting the special-cubic mixture model is only appropriate if the total amount does not affect the response, while fitting (4.3) is only appropriate if the nonlinear blending is quadratic and the total amount has a linear effect on the response (but does not affect the component blending properties). Hence, by taking a one-half fraction of the complete design for q = 3 and r = 2, we forfeit the ability to detect whether or not the total amount affects the component blending.

As a second example, consider the one-half fraction of the four-component simplex-centroid x 2 mixture-amount design which is listed in Table 4.3 and is pictured in Figure 4.5. This 15-point design supports fitting the 15-term mixture model

$$\eta = \sum_{i=1}^{4} \beta_i^0 x_i + \sum_{i<j}^{4} \beta_{ij}^0 x_i x_j + \sum_{i<j<k}^{4} \beta_{ijk}^0 x_i x_j x_k + \beta_{1234}^0 x_1 x_2 x_3 x_4 \quad , \tag{4.4}$$

or the 15-term mixture-amount models

$$\eta = \sum_{i=1}^{4} \beta_i^0 x_i + \sum_{i<j}^{4} \beta_{ij}^0 x_i x_j$$

$$+ \sum_{i<j<k}^{4} \beta_{ijk}^0 x_i x_j x_k + \beta_0^1 A' \qquad (4.5)$$

or

$$\eta = \sum_{i=1}^{4} \beta_i^0 x_i + \sum_{i<j}^{4} \beta_{ij}^0 x_i x_j$$

$$+ \sum_{i=1}^{4} \beta_i^1 x_i A' + \{\text{one } \beta_{ij}^1 x_i x_j A' \text{ term}\} \quad . \qquad (4.6)$$

These three models are appropriate under different assumptions about component blending and how the total amount affects the response, if at all. Model (4.6) is the only one of the three that allows for the component blending properties being affected by total amount, and does so at the cost of assuming there is no special cubic or quartic blending among the four components. Since the face centroids (1/3,1/3,1/3,0), . . . , (0,1/3,1/3,1/3) and the overall centroid (1/4,1/4,1/4,1/4) are included in the simplex-centroid design for the purpose of estimating the special cubic and quartic blending properties, it seems apparent that the one-half fraction (in Table 4.3), is not optimal for fitting model (4.6). That this indeed is the case is noted by observing that one could do better by replacing the face and overall centroids with the remaining

Table 4.3. One-Half Fraction[a] of a Simplex-Centroid x 2 Mixture-Amount Design for Four Components

x_1	x_2	x_3	x_4	A'
1/2	1/2	0	0	-1
1/2	0	1/2	0	-1
1/2	0	0	1/2	-1
0	1/2	1/2	0	-1
0	1/2	0	1/2	-1
0	0	1/2	1/2	-1
1/4	1/4	1/4	1/4	-1
1	0	0	0	1
0	1	0	0	1
0	0	1	0	1
0	0	0	1	1
1/3	1/3	1/3	0	1
1/3	1/3	0	1/3	1
1/3	0	1/3	1/3	1
0	1/3	1/3	1/3	1

(a) Fraction obtained using I = +ABCDE as the defining contrast. Switching the levels of A' yields the I = -ABCDE fraction.

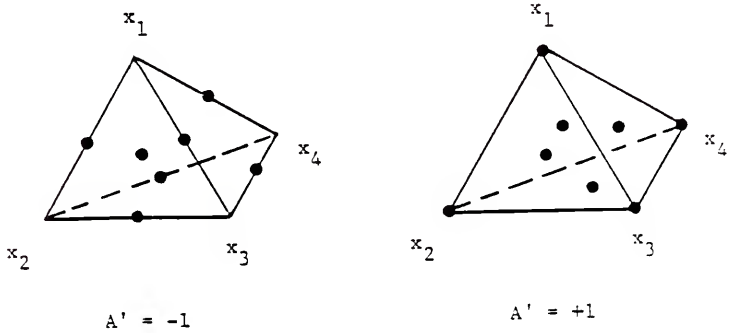


Figure 4.5. Graphical Display of Design in Table 4.3

vertex points and another edge centroid (see later in this section for a discussion of such designs).

The above two examples illustrate that the second fractionation method of Scheffé can be used to fractionate the simplex-centroid x 2 mixture-amount designs. However, depending on the type of component blending to be investigated, these fractions provide at best a portion of the information about the effects of total amount on component blending and at worst no information about the effect of A on the response. If all higher order component blending terms (such as cubic, quartic, . . .) are to be included in the model, these fractions provide no information about how the total amount affects the response (if at all). If some of the higher order component blending properties may be assumed to be negligible, then these fractions do provide some information about how the total amount affects the response (or the component blending). However, for situations in which higher order component blending properties are assumed to be negligible, fractional designs with better characteristics than those provided by the method of Scheffé can be obtained using a computer-aided design approach. One such approach based on D_N-optimality is discussed below.

The fractionation methods discussed so far are applicable only for certain types of mixture-amount designs. However, the computer-aided design approach, introduced in

Section 1.1, provides a method for fractionating any mixture-amount design for both unconstrained and constrained mixture-amount experiments. Recall that the computer-aided design approach involves choosing a criterion of interest (e.g., D_N, G_N, V_N, or A_N-optimality) and then selecting points for the design from a candidate list so as to optimize the design criterion chosen. For design fractionation purposes, the candidate points are the points of any mixture-amount design to be fractionated. The D_N-optimality criterion (which seeks to maximize $\det(X'X)$, where X is the N-point expanded design matrix associated with the mixture-amount model to be fitted) is chosen for this work because of its popularity and the availability of Mitchell's (1974) DETMAX computer program to implement it. Although the DETMAX algorithm does not guarantee generation of a D_N-optimal design, it often does so; when it does not, the resulting design is near D_N-optimal.

We discuss the development of D_N-optimal designs for canonical polynomial mixture-amount models. The development for other families of mixture-amount models proceeds in much the same way.

The candidate points for a given design/model are usually the points of the associated complete mixture-amount design. Several examples are given below.

- The candidate points for the models (A1) - (A5) in Appendix A are (assuming an unconstrained mixture-amount experiment) the simplex vertices at each

level of total amount. Since there are no nonlinear blending terms in these models, the D_N-optimal design will not contain binary, ternary, . . . , etc. mixtures even if included in the candidate list. For a constrained mixture-amount experiment, the candidate points would consist of the constraint region vertices at each level of total amount.

- The candidate points for models (A6) - (A14) in Appendix A are (for an unconstrained mixture-amount experiment) the simplex vertices (1,0, . . . ,0), . . . , (0,0, . . . ,1) and the edge centroids (.5,.5,0, . . . ,0), . . . , (0, . . . ,0,.5,.5). The face centroids (1/3,1/3,1/3,0, . . . ,0), . . . , (0,0, . . . ,1/3,1/3,1/3) would be included if the mixture-amount model under consideration contains special cubic terms. For a constrained mixture-amount experiment, the candidate points would consist of the constraint region vertices and edge centroids at each level of total amount. The two-dimensional face centroids would be included if the mixture-amount model contains special cubic terms.

- The candidate points for a full cubic canonical polynomial mixture-amount model in an unconstrained mixture-amount experiment are the points of a {q,3} simplex-lattice at each level of total amount.

The D_N-optimal (or near D_N-optimal) designs for several of the canonical polynomial mixture-amount models of Appendix A were obtained using the DETMAX program for three component unconstrained mixture-amount experiments with two and three levels of total amount. Some of the many possible D_N-optimal designs for the models considered are given in Appendix C. The results for q = 3 suggest procedures for developing D_N-optimal designs (without the need of a computer program such as DETMAX) for unconstrained

mixture-amount experiments for all values of $q \geq 3$. The procedures for two levels of amount are given in Tables 4.4 - 4.9 and for three levels of amount in Tables 4.10 - 4.12. The following terms are used in these tables:

- positions--The possible geometric locations of the design points regardless of the level of total amount.
- point--A specific candidate point chosen for the design.
- full set--All candidate points included exactly once in the design.

The procedures in Tables 4.4 - 4.12 are written in a way that facilitates the generation of a sequence of D_N-optimal designs as N increases, with each design being obtainable by adding one or more points to the preceding design. The designs from Figures C.1 - C.9 in Appendix C serve as examples of the procedures in Tables 4.4 - 4.12 for the case $q = 3$.

The procedures in Tables 4.4 - 4.12 describe how to generate D_N-optimal designs for $p \leq N \leq C+p$, where p is the number of parameters in the particular model and C is the number of candidate points for the design. For each of the nine models considered, an $N = C+p$ design consists of the C candidate points plus an $N = p$ design. Hence, the procedures cycle and are applicable for developing D_N-optimal designs for any value of $N \geq p$.

Table 4.4. Sequential D_N-Optimal Design Development Procedure for Model (A6) in Appendix A

Candidate Points

Simplex vertices and edge centroids at the two levels of A (assumed coded as -1 and +1). There are $C = q(q+1)$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \beta_0^1 A'$$

N	Procedure*
$p = \frac{q(q+1)}{2} + 1$	The smallest possible D_N-optimal design for this model contains p points that cover all positions once with one position covered twice (once at each of the two levels of A). The positions covered once may be at either of the two levels of A.
p+1 to C	Add points to cover the remaining positions at each level of A (without replicating points) until a full set of candidate points is obtained.
C+1 to C+p	Add additional points to cover each position once. Note that an N = C+p design is a full set plus an N = p design. Hence, the procedure cycles, continuing as above.

* See Figure C.1 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.5. Sequential D_N-Optimal Design Development Procedure for Model (A7) in Appendix A

Candidate Points

Simplex vertices and edge centroids at the two levels of A (assumed coded as -1 and +1). There are $C = q(q+1)$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A'$$

N	Procedure*
$p = \frac{q(q+1)}{2} + q$	The smallest possible D_N-optimal design for this model contains the vertices at both levels of A and points which cover the edge centroid positions once. The edge centroids may be chosen at either level of amount so long as each position is covered.
p+1 to C	Add the remaining edge centroid points until a full set of candidate points is obtained.
C+1 to C+2p	Add additional points to cover each vertex position once, then twice (without replicating among the additional points). These points serve as second replicates of the vertex positions at each level of A.
C+2q+1 to C+p	Add points to cover each edge centroid position once. Note that an N = C+p design is just a full set of candidate points plus an N = p design. Hence, the procedure cycles, continuing as above.

* See Figure C.2 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.6. Sequential D_N-Optimal Design Development Procedure for Model (A8) in Appendix A

Candidate Points

Simplex vertices and edge centroids at the two levels of A (assumed coded as -1 and +1). There are $C = q(q+1)$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \beta_{ij}^1 x_i x_i A'$$

N	Procedure*
$p = C$	The smallest possible D_N-optimal design for this model consists of a full set of candidate points.
C+1 to 2C	Add additional points until a second full set is obtained. In choosing additional points, it is not necessary to cover each position once before covering a position twice (once at each of the two levels of A). However, points should not be replicated within the additional points. Note that the procedure cycles, continuing as above.

* See Figure C.3 in Appendix C for examples of designs generated by this procedure for the case $q = 3$.

Table 4.7. Sequential D_N-Optimal Design Development Procedure for the Special-Cubic by Constant Mixture-Amount Model Below

Candidate Points

Simplex vertices, edge centroids, and two dimensional face centroids at the two levels of A (assumed coded as -1 and +1). There are $C = (q^3+5q)/3$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i<j<k}^{q} \beta_{ijk}^0 x_i x_j x_k + \beta_0^1 A'$$

N	Procedure*
$p = C/2 + 1$	The smallest possible D_N-optimal design for this model contains points that cover all positions once with one position covered twice.
p+1 to C	Add points to cover the remaining positions twice (without replicating points) until a full set of candidate points is obtained.
C+1 to C+p	Add additional points to cover each position once. Note that an N = C+p design is just a full set plus an N = p design. Hence, the procedure cycles, continuing as above.

* See Figure C.4 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.8. Sequential D_N-Optimal Design Development Procedure for the Special-Cubic by Linear Mixture-Amount Model Below

Candidate Points

Simplex vertices, edge centroids, and two dimensional face centroids at the two levels of A (assumed coded as -1 and +1). There are $C = (q^2+5q)/3$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i<j<k}^{q} \beta_{ijk}^0 x_i x_j x_k + \sum_{i=1}^{q} \beta_i^1 x_i A'$$

N	Procedure*
$p = C/2 + q$	The smallest possible D_N-optimal design for this model contains points chosen to cover all positions once and the vertices twice (once at each of the two levels of A).
$p+1$ to $p+\binom{q}{2}$	Add the remaining edge centroids.
$p+\binom{q}{2}+1$ to C	Add the remaining face centroids until a full set of candidate points is obtained.
C+1 to C+2q	Add additional points to cover the vertex positions once, then twice.
C+2q+1 to $C+2q+\binom{q}{2}$	Add additional points to cover the edge centroid positions once.
$C+2q+\binom{q}{2}+1$ to C+p	Add additional points to cover the face centroid positions once. Note that an N = C+p design is just a full set of candidate points plus an N = p design. Hence, the procedure cycles, continuing as above.

* See Figure C.5 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.9. Sequential D_N-Optimal Design Development Procedure for the Special-Cubic by Linear Mixture-Amount Model Below

Candidate Points

Simplex vertices, edge centroids, and two dimensional face centroids at the two levels of A (assumed coded as -1 and +1). There are $C = (q^2+5q)/3$ candidate points.

Model

$$\eta = \sum_{h=0}^{1} \left[\sum_{i=1}^{q} \beta_i^h x_i + \sum_{i<j}^{q} \beta_{ij}^h x_i x_j + \sum_{i<j<k}^{q} \sum \beta_{ijk}^h x_i x_j x_k \right] (A')^h$$

N	Procedure*
p = C	The smallest possible D_N-optimal design for this model consists of a full set of candidate points.
C+1 to 2C	Add additional points until a second full set is obtained. In choosing additional points, it is not necessary to cover each position once before covering a position twice (once at each of the two levels of A). However, points should not be replicated within the additional points. Note that the procedure cycles, continuing as above.

* See Figure C.6 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.10. Sequential (Near)D_N-Optimal Design Development Procedure for Model (A12) in Appendix A

Candidate Points

Simplex vertices and edge centroids at the three levels of A (assumed coded as -1, 0, and +1). There are $C = 3q(q+1)/2$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i=1}^{q} \beta_i^2 x_i (A')^2$$

N	Procedure*
$p = \frac{q(q+1)}{2} + 2q$	The smallest possible D_N-optimal design for this model contains the vertices at all three levels of A and covers the edge centroid positions once.
$p+1$ to $p+\binom{q}{2}$	Add points to cover the edge centroid positions twice. Two edge centroids at each of the three levels of A gives the smallest variances for parameter estimates.
$p+\binom{q}{2}+1$ to C	Add the remaining edge centroids to complete a full set of candidate points.
$C+1$ to $C+3q$	Add vertex points until all vertices are included again (replicated twice). Slightly larger determinants are obtained if one first covers the q vertex positions once, then twice, and finally three times (all vertices). Variances of the β^0 and β^2 are smaller if the vertex points are concentrated at $A' = 0$, while the variances of the β^1 are smaller if the vertex points are concentrated at $A' = -1$ and $A' = +1$.

Table 4.10.-continued.

N	Procedure*
C+3q+1 to C+p	Add points to cover the edge centroid positions once. Note that an N = C+p design is just a full set of candidate points plus an N = p design. Hence, the procedure cycles, continuing as above.

* See Figure C.7 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.11. Sequential (Near)D_N-Optimal Design Development Procedure for Model (A13) in Appendix A

Candidate Points

Simplex vertices and edge centroids at the three levels of A (assumed coded as -1, 0, and +1). There are $C = 3q(q+1)/2$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \beta_{ij}^1 x_i x_j A' + \sum_{i=1}^{q} \beta_i^2 x_i (A')^2$$

N	Procedure*
$p = q^2 + 2q$	The smallest possible D_N-optimal design for this model contains the vertices at all three levels of A plus the edge centroids on the A' = -1 and A' = +1 simplexes.
p+1 to C	Add edge centroids on the A' = 0 simplex to obtain a full set of candidate points.
C+1 to C+2q	Add vertices on the A' = -1 and A' = +1 simplexes. Slightly larger determinants are obtained if one first covers the q vertex positions once, then twice.
$(3q^2+7q+2)/2$ to $6q+4\binom{q}{2}-1$	Designs for N in this range are not easy to describe. They are not sequentially obtainable from the above designs as they do not contain a full set of candidate points. See Figure C.8 in Appendix C for some examples when q = 3.

Table 4.11.-continued.

N	Procedure*
$6q + 4\binom{q}{2}$	This unique design consists of the vertices at all three levels of A twice, and the edge centroids on the A' = -1 and A' = +1 simplexes twice. Note that it does not contain a full set of candidate points.
$6q+4\binom{q}{2}+1$ to C+p	Add edge centroids on the A' = 0 simplex. Note that an N = C+p design is just a full set of candidate points plus an N = p design. Hence, the procedure cycles, continuing as above.

* See Figure C.8 in Appendix C for examples of designs generated by this procedure for the case q = 3.

Table 4.12. Sequential D_N-Optimal Design Development Procedure for Model (A14) in Appendix A

Candidate Points

Simplex vertices and edge centroids at the three levels of A (assumed coded as -1, 0, and +1). There are $C = 3q(q+1)/2$ candidate points.

Model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \beta_{ij}^1 x_i x_j A'$$

$$+ \sum_{i=1}^{q} \beta_i^2 x_i (A')^2 + \sum_{i<j}^{q} \beta_{ij}^2 x_i x_j (A')^2$$

N	Procedure*
$p = C$	The smallest possible D_N-optimal design for this model consists of one full set of candidate points.
C+1 to C+p	Add additional points until a second full set is obtained. It is not necessary to cover all positions once (or twice) before covering some positions twice (or three times). Concentrating the new points on the $A' = -1$ and $A' = +1$ simplexes lowers the variances of the β^1, while concentrating points on the $A' = 0$ simplex lowers the variances of the β^0 and β^2. For larger N, the procedure cycles, continuing as above.

* See Figure C.9 in Appendix C for examples of designs generated by this procedure for the case q = 3.

A potential criticism for the use of D_N-optimal designs is that they are specific to the model under consideration. However, this is not totally true here. To see this, consider the procedures in Tables 4.4 - 4.6 and note that the procedures in Tables 4.4 and 4.5 are more complicated (restrictive) than the procedure of Table 4.6. The simplicity of the procedure in Table 4.6 is a result of the associated mixture-amount model having x_iA' and x_ix_jA' terms corresponding to the x_i and x_ix_j terms. The models in Tables 4.4 and 4.5 are reduced forms of the model in Table 4.6 and do not have this "symmetry of terms" property. The "nonsymmetry of terms" for the models in Tables 4.4 and 4.5 is why the corresponding procedures for developing D_N-optimal designs are not as straightforward as the procedure of Table 4.6. The point of this discussion is that designs developed by the more restrictive procedures in Tables 4.4 and 4.5 also satisfy the procedure of Table 4.6; that is, the procedures of Tables 4.4 and 4.5 generate designs that are not only D_N-optimal for their corresponding models, but are also D_N-optimal for the model of Table 4.6. This is true only for designs containing $N \geq C$ points, since a minimum of C points is needed to support fitting the model of Table 4.6.

On the other hand, designs generated by the procedure of Table 4.4 are in general not D_N-optimal for the model of Table 4.5 (and vice versa), although it may be possible to

construct such designs for certain values of N. As an example, when q = 3 the designs for $9 \leq N \leq 14$ displayed in the first design columns of Figures C.1 and C.2 are D_N-optimal for the models of both tables.

The above discussion uses the procedures and models of Tables 4.4, 4.5, and 4.6 to illustrate that D_N-optimal designs obtained by using these procedures may be optimal for more than one model. Similar results hold for the procedures and models of Tables 4.7 - 4.12; specifically,

- the procedures of Tables 4.7 and 4.8 yield designs that are also D_N-optimal for the model of Table 4.9
- the procedures of Tables 4.10 and 4.11 yield designs that are also D_N-optimal for the model of Table 4.12.

It is clear from the procedures in Tables 4.4 - 4.12 (and the examples for the case q = 3 in Appendix C) that there is often more than one D_N-optimal design for a given model and value of N. To choose among several such designs, we might consider other properties or characteristics of the designs. One characteristic already considered is whether the design is D_N-optimal for more than one model. Another design characteristic that might be of interest is how the parameter estimators depend on the observations at the design points. For many designs, some of the parameter estimators will depend on the form of the model while others may not. It might also be of interest to consider the

parameter estimator variances. Properties of interest might be criterion based measures such as $tr[(X'X)^{-1}]$, $max[\underline{x}'(X'X)^{-1}\underline{x}]$, or $avg[\underline{x}'(X'X)^{-1}\underline{x}]$, where the maximum or average is computed over the candidate points. Examples of how these characteristics and properties might be used to choose among several D_N-optimal designs are given in Appendix D for some of the three-component designs from Appendix C.

The D_N-optimal computer-aided design approach can also be used to fractionate designs for constrained mixture-amount experiments. However, because of the unlimited ways in which the mixture component proportions can be constrained, it is not possible to develop general procedures as we did for unconstrained mixture-amount experiments. One must have and use a computer program (such as DETMAX) for each particular application. As an example, consider the three component constrained mixture-amount design given earlier in Table 4.1 (and pictured in Figure 4.3). Fractions of this design for several values of N are presented graphically in Figure 4.6. The designs were obtained using DETMAX for the special-cubic by linear mixture-amount model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \beta_{ij}^0 x_i x_j + \beta_{123}^0 x_1 x_2 x_3 + \sum_{i=1}^{3} \beta_i^1 x_i A' \quad . \quad (4.7)$$

To summarize, in this section we have discussed several techniques for fractionating mixture-amount designs for

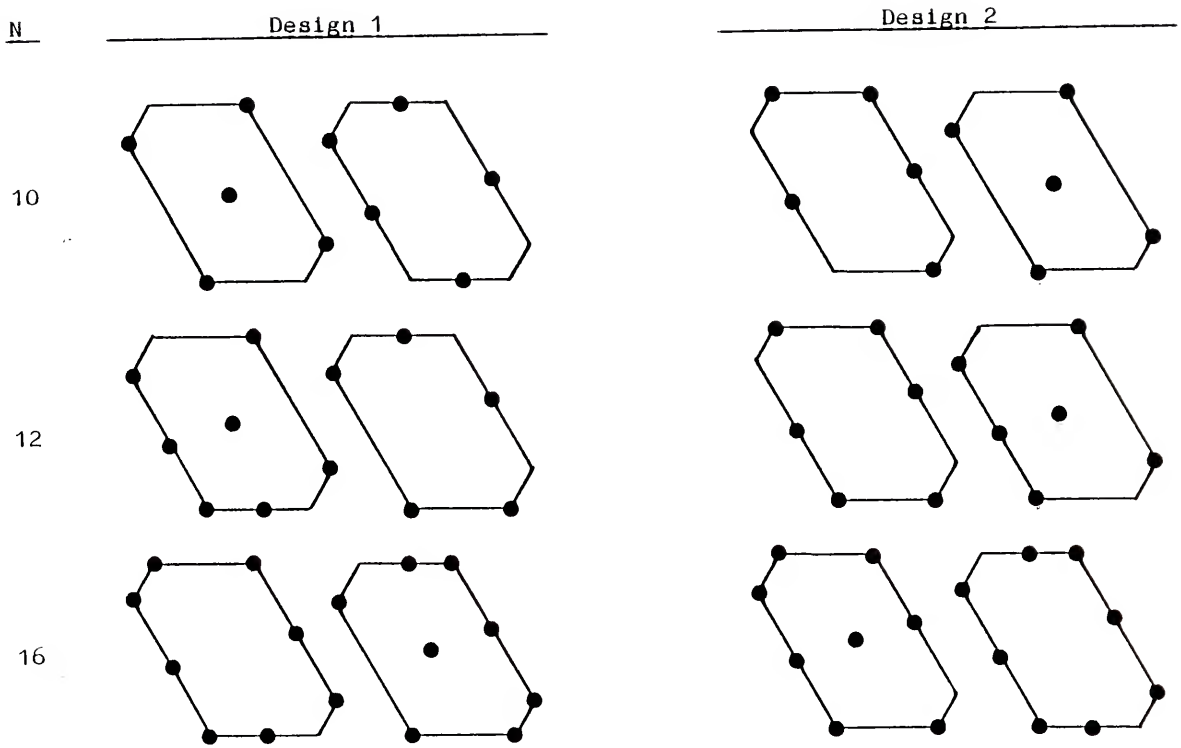


Figure 4.6. DETMAX Designs for the Constrained Mixture-Amount Experiment Listed in Table 4.1

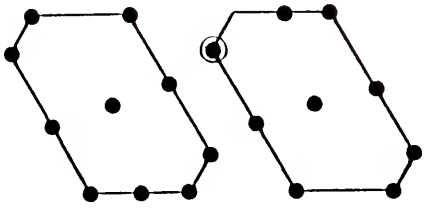
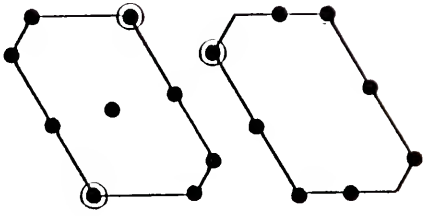
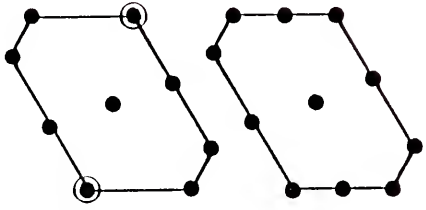
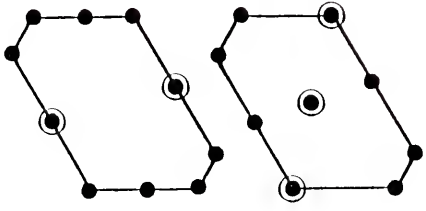
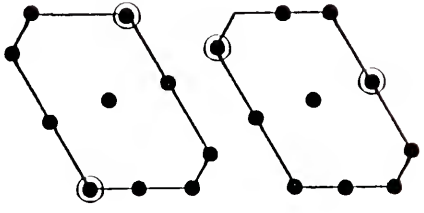
N	Design 1	Design 2
20		
22		The pattern of the design to the left is unique, and yields $\det(X'X) = 9.7 \times 10^{-15}$. The full set of 22 candidate points yields $\det(X'X) = 9.1 \times 10^{-15}$.
24		

Figure 4.6.-continued.

unconstrained mixture-amount experiments, including a computer-aided design approach. This approach was also used to fractionate a constrained mixture-amount design. It is clear that the computer-aided design approach is quite powerful and can be used to fractionate any mixture-amount design (including the ratio or log-ratio variable designs). The D_N-optimality criterion was chosen for use here because of its popularity and the availability of the DETMAX program (Mitchell 1974) to implement it.

CHAPTER FIVE
MODELS AND DESIGNS BASED ON THE COMPONENT AMOUNTS

Mixture-amount experiments, introduced in the previous chapter, were seen to be a type of general mixture experiment in which the experimenter wishes to understand not only how the components blend with one another, but also if and how the amount of the mixture affects the component blending. Mixture-amount models and designs were formulated in terms of the component proportions and the levels of total amount of the mixture in such a way as to provide this information to the experimenter. However, oftentimes experimenters formulate their questions concerning the effects of the components on the response by expressing their models and designs in terms of the amounts of individual components. For example, in a fertilizer study the experimenter may only want to know how much of each component is to be present in the fertilizer in order to maximize the crop yield.

In this chapter, we shall discuss two types of general mixture experiments where the models and designs may be expressed in terms of the component amounts. For each type of experiment, the respective designs and models are mentioned.

5.1 Standard Designs and Polynomial Models Based on the Component Amounts

Let us consider an experimental approach in which the controllable variables are the amounts of the individual components, denoted by a_i, $i=1,2, \ldots ,q$. Typically, an experimenter wishing to model the response as a function of the individual component amounts, would select either a first or second-degree polynomial model of the form

$$\eta = \alpha_0 + \sum_{i=1}^{q} \alpha_i a_i \tag{5.1}$$

$$\eta = \alpha_0 + \sum_{i=1}^{q} \alpha_i a_i + \sum_{i=1}^{q} \alpha_{ii} a_i^2 + \sum_{i<j}^{q} \sum \alpha_{ij} a_i a_j \, . \tag{5.2}$$

Similar models are obtained by substituting $\log a_i$ (or other functions of the a_i) for the a_i in (5.1) and (5.2). These models, or those in (5.1) and (5.2), would be fitted to data collected at the points of any standard response surface design (as discussed in Section 1.1). Studies of this type were performed by Hader et al. (1957), Moore et al. (1957), Suich and Derringer (1977), and Valencia (1983).

An experiment conducted using the above standard design, component amount model approach will be referred to as a component amount (CA) experiment. A component amount experiment is a type of general mixture experiment (as defined in Section 1.3). To see this, first note that the amount of an individual component (a_i) may be written as the

product of the proportion of the component in the mixture (x_i) and the total amount of the mixture (A): $a_i = x_i A$, $i=1,2, \ldots ,q$. Although the response in a component amount experiment is nominally assumed to be a function of the component amount variables, the relationship $a_i = x_i A$ allows us to view the response as a function of the component proportions and the total amount of the mixture, i.e.,

$$\begin{aligned} \eta &= f(a_1,a_2,\ldots,a_q) \\ &= f(x_1A,x_2A,\ldots,x_qA) \\ &= g(x_1,x_2,\ldots,x_q,A) \ . \end{aligned} \tag{5.3}$$

Recalling the definition (in Section 1.3) of a general mixture experiment as one in which the response is assumed to be a function of the component proportions and possibly the total amount of the mixture, (5.3) shows that a component amount experiment is a type of general mixture experiment.

It is of interest to note that the component amount variables a_i in a component amount experiment are mathematically independent. A type of experiment formulated in terms of the component amounts where this is not the case is discussed in the next section.

5.2 Models and Designs for Experiments Where the Component Amounts Have a Mixture-Like Restriction

A different experimental approach based on the component amounts is discussed in this section. This approach arises in situations where the possible combinations of component amounts are restricted by a linear constraint on the a_i. The approach is introduced with the following hypothetical two-component example.

A soft-drink company would like to determine the blend of two artificial sweeteners (S1 and S2, say) that yields the best taste (minimum intensity of aftertaste) when used in a diet drink. From previous experience, the company knows that the optimum amounts of the individual sweeteners S1 and S2 when used alone in the drink are 9 and 12 mg/fl.oz., respectively. An experiment is set up where average aftertaste rating values are collected from the combinations of the two sweeteners (a_1,a_2) = (9,0), (6.75,3), (4.5,6), (2.25,9), and (0,12). The data collected are to be used for fitting the model

$$\eta = \alpha_1 a_1 + \alpha_1 a_2 + \alpha_{12} a_1 a_2 , \qquad (5.4)$$

which will in turn be used to determine the best combination of sweeteners S1 and S2.

To see what makes this experimental approach different from the mixture-amount and component amount approaches,

first consider the plot of the sweetener combinations given in Figure 5.1. The combinations all lie on the line

$$a_2 = (-4/3)a_1 + 12 \ . \tag{5.5}$$

The company has chosen a desired sweetness level based on the amounts $a_1 = 9$ and $a_2 = 12$, and the level is constant on the line (5.5). They wish only to consider combinations of the sweeteners along this line. The line (5.5) places a restriction on the amounts a_1 and a_2 of the two sweeteners and thus they are not mathematically independent as is the case with the component amount variables in the component amount approach.

The restriction (5.5) on the component amount variables, rewritten as

$$a_1/9 + a_2/12 = 1 \ , \tag{5.6}$$

is reminiscent of the restriction $\sum_{i=1}^{q} x_i = 1$ in a mixture or mixture-amount experiment. Since the total amounts of the five combinations chosen for the experiment are different, it is natural to compare this approach to the mixture-amount approach. There is a clear difference between the two approaches; with a mixture-amount approach the component blends are performed at each of two or more levels of total amount, while with this approach each blend (combination) is performed at exactly one amount.

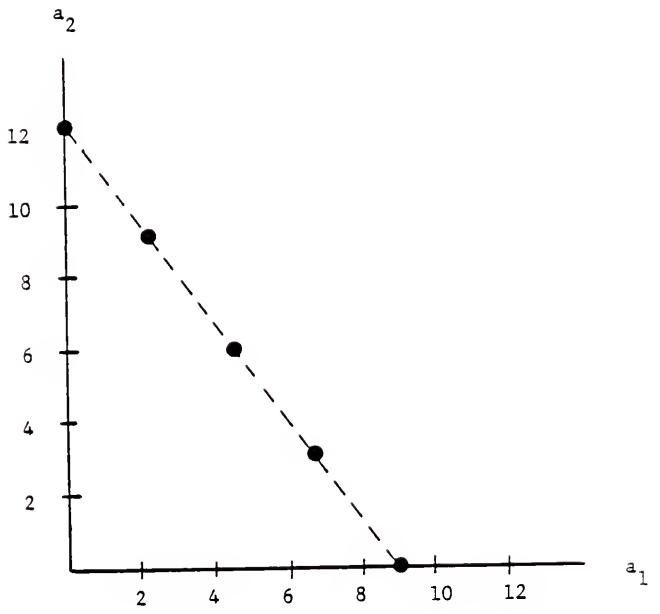


Figure 5.1. Combinations of Two Sweeteners in the Soft Drink Example

The restriction (5.6) [or equivalently (5.5)], when applied to the second-degree model (5.2), results in the intercept term and the a_1^2 and a_2^2 terms being redundant, thus producing (5.4). To see this, consider the usual second-degree polynomial model

$$\eta = \gamma_0 + \gamma_1 a_1 + \gamma_2 a_2 + \gamma_{11} a_1^2 + \gamma_{22} a_2^2 + \gamma_{12} a_1 a_2 . \quad (5.7)$$

Substituting $\gamma_0 = \gamma_0(1) = \gamma_0(a_1/9 + a_2/12)$, $a_1^2 = a_1(a_1) = a_1[9 - (3/4)a_2]$ and $a_2^2 = a_2(a_2) = a_2[12 - (4/3)a_1]$ into (5.7) yields

$$\begin{aligned}
\eta &= \gamma_0(a_1/9+a_2/12) + \gamma_1 a_1 + \gamma_2 a_2 + \gamma_{11} a_1[9-3a_2/4] \\
&\quad + \gamma_{22} a_2[12-4a_1/3] + \gamma_{12} a_1 a_2 \\
&= (\gamma_0/9 + \gamma_1 + 9\gamma_{11})a_1 + (\gamma_0/12 + \gamma_2 + 12\gamma_{22})a_2 \\
&\quad + [\gamma_{12} - (3/4)\gamma_{11} - (4/3)\gamma_{22}]a_1 a_2 \\
&= \alpha_1 a_1 + \alpha_2 a_2 + \alpha_{12} a_1 a_2 ,
\end{aligned}$$

where $\alpha_1 = (\gamma_0/9 + \gamma_1 + 9\gamma_{11})$, $\alpha_2 = (\gamma_0/12 + \gamma_2 + 12\gamma_{22})$, and $\alpha_{12} = [\gamma_{12} - (3/4)\gamma_{11} - (4/3)\gamma_{22}]$. Hence, equation (5.7) reduces to the form (5.4) when the restriction (5.6) is applied.

So far, the approach illustrated by the sweetener example has been presented in terms of the component amounts. However, the restriction (5.6) and its similarity

to the mixture restriction $\sum_{i=1}^{q} x_i = 1$ suggests a transformation of variables given by

$$x_1^* = a_1/9 \quad \text{and} \quad x_2^* = a_2/12 \ , \tag{5.8}$$

where x_1^* = the proportion of 9 mg/fl.oz. of S1 used in a combination of sweeteners, and x_2^* = the proportion of 12 mg/fl.oz. of S2 used in a combination of sweeteners. Under the transformation (5.8), the restriction (5.6) becomes $x_1^* + x_2^* = 1$, and the model (5.4) becomes

$$\eta = \delta_1 x_1^* + \delta_2 x_2^* + \delta_{12} x_1^* x_2^* \ , \tag{5.9}$$

where $\delta_1 = 9\alpha_1$, $\delta_2 = 12\alpha_2$, and $\delta_{12} = 9(12)\alpha_{12}$. The combinations in the sweetener experiment in the transformed variables (x_1^*, x_2^*) are (1,0), (.75,.25), (.5,.5), (.25,.75), and (0,1). Hence, this approach is analogous to a mixture experiment, where x_1^* and x_2^* are proportions of the components relative to the pure component amounts (compared to the usual mixture proportions which are relative to the total amount of the mixture). We will henceforth refer to proportions such as x_1^* and x_2^* as <u>component-wise proportions</u>.

The sweetener example above served to illustrate several features of the type of experimental approach to be discussed in this section. We now generalize this approach and its features for other types of applications and for more than two components.

In general, suppose we have q components and wish to determine the component amounts a_1, a_2, . . . , a_q that optimize the response of interest. The allowable amount combinations are fractions of specified pure component amount values a_1^0, a_2^0, . . . , a_q^0, where the fractions for a given combination must sum to unity [see equation (5.16) later]. The pure component amount values a_i^0, i=1,2, . . . ,q, (henceforth referred to as base values) are specified by the experimenter and are typically assumed to produce a desirable response value or to satisfy some other characteristic required of all combinations. In the sweetener example, the base values $a_1^0 = 9$ and $a_2^0 = 12$ were chosen because they provide an equal degree of sweetness (which was not the response of interest). In some drug and insecticide experiments, the base values are chosen so that the pure components at their base amounts produce equal (or nearly equal) response values; in such experiments, the base values are referred to as equivalent doses. In other drug or insecticide experiments, the base values may be the highest doses of the pure components that can be used without causing toxicity problems for the patient (in drug studies) or to the environment (in insecticide experiments).

Whatever the reason for their existence in a given situation, the base values a_1^0, a_2^0, . . . , a_q^0 impose a restriction on those compositions $(a_1, a_2, \ldots, a_q)$ that can be investigated. This restriction may be written in the

general form

$$\sum_{i=1}^{q} g_i a_i = 1 \ , \tag{5.10}$$

where $g_i = 1/a_i^0$, i=1,2, . . . ,q. This restriction is in addition to the natural constraints

$$0 \leq a_i \leq a_i^0 \ , \ i=1,2,\ldots,q \ . \tag{5.11}$$

In some situations, the a_i may be constrained by lower and/or upper bounds

$$0 \leq l_i \leq a_i \leq u_i \leq a_i^0 \ , \ i=1,2,\ldots,q \ . \tag{5.12}$$

Because of restriction (5.10), reduced polynomial forms such as

$$\eta = \sum_{i=1}^{q} \alpha_i a_i \tag{5.13}$$

and

$$\eta = \sum_{i=1}^{q} \alpha_i a_i + \sum_{i<j}^{q} \sum \alpha_{ij} a_i a_j \tag{5.14}$$

must be used to model the data.

Consider the variable transformation given by

$$x_i^* = \frac{a_i}{a_i^0}, \quad i=1,2,\ldots,q \ , \tag{5.15}$$

recalling that the base values a_i^0 are fixed for each i. The x_i^* are referred to as component-wise proportions. By applying the transformation (5.15), restrictions (5.10), (5.11), and (5.12) reduce to

$$\sum_{i=1}^{q} x_i^* = 1 \ , \tag{5.16}$$

$$0 \leq x_i^* \leq 1, \quad i=1,2,\ldots,q \ , \tag{5.17}$$

and

$$0 \leq l_i^* \leq x_i^* \leq u_i^* \leq 1, \quad i=1,2,\ldots,q. \tag{5.18}$$

These restrictions are similar to the restrictions used in unconstrained and constrained mixture experiments. The similarity of the restrictions suggests that mixture-type designs in the x_i^* may be utilized for experiments of this kind. Because mixture designs for both unconstrained and constrained problems were presented in Section 2.2, they are not discussed again here.

Under the transformation (5.15), the models (5.13) and (5.14) become

$$\eta = \sum_{i=1}^{q} \delta_i x_i^* \tag{5.19}$$

and

$$\eta = \sum_{i=1}^{q} \delta_i x_i^* + \sum_{i<j}^{q} \sum \delta_{ij} x_i^* x_j^* \, . \tag{5.20}$$

The interpretations of the parameters in these models are given by:

δ_i = the expected response to component i in the amount a_i^0,

δ_{ij} = the expected nonlinear blending effect of components i and j having the base amounts a_i^0 and a_j^0, respectively.

These interpretations are slightly different from those of the corresponding parameters in Scheffé canonical polynomial mixture models in that the interpretations of the mixture model parameters are not linked to base component amount values as are the interpretations of the δ_i and δ_{ij} parameters above.

The similarity of models (5.19) and (5.20) to the corresponding Scheffé canonical polynomial mixture models suggests that models in the x_i^* analogous to any of the mixture model forms presented in Section 2.1 could be considered here. Designs corresponding to these models, which were presented in Section 2.2, are also applicable for this approach.

Up until now, the experimental approach discussed in this section has probably almost always been implemented in practice using models and designs based on the component amount variables a_i. We have shown that the approach may equivalently be implemented using models and designs based on the component-wise proportions x_i^* (given the base values a_i^0). Regardless of the implementation used, this experimental approach is a type of general mixture experiment since the response is assumed to be a function of the component amounts [directly in models such as (5.13) and (5.14), or indirectly in models such as (5.19) and (5.20) through the transformation (5.15)]. As we saw by equation (5.3) in Section 5.1, a response assumed to be a function of the component amounts may also be considered as a function of the component proportions and the total amount of the mixture.

We will refer to the type of general mixture experiment discussed in this section as a component-wise mixture (CWM) experiment. Comparisons among the mixture-amount, component amount, and component-wise mixture experimental approaches are made in Chapter 6.

CHAPTER SIX
COMPARISON OF MIXTURE-AMOUNT, COMPONENT AMOUNT, AND COMPONENT-WISE MIXTURE EXPERIMENTS

In the previous three chapters, three different types of general mixture experiments were discussed: mixture-amount, component amount, and component-wise mixture experiments. While all three types of experiments involve mixtures of components at varying total amounts, the design and modeling approaches used for each type of experiment are different. In this chapter, we compare the three approaches and discuss the similarities and differences among them.

6.1 Comparison of Constraint Regions

For each of the three approaches (mixture-amount, component amount, and component-wise mixture), the component proportions, component amounts, and the total amount of a mixture are all constrained in some way, either explicitly or implicitly. It is of interest to consider the explicit and implicit constraint regions for each of the three approaches and see how they compare.

The usual (explicit) constraints for each of the three approaches are summarized in Table 6.1. The constraint regions defined by the constraints in Table 6.1 have the

following characteristics:

Type Region	Configuration	Dimensionality
Mixture-Amount	Regular (q-1)-dimensional simplex or irregular hyperpolyhedron extended orthogonally in the qth dimension.	q
Component Amount	Rectangular.	q
Component-Wise Mixture	Irregular simplex or irregular hyperpoly-hedron.	q-1

The most striking difference in these characteristics is that the dimensionality of the component-wise mixture constraint region is one less than for the mixture-amount and component amount constraint regions. Although the mixture-amount and component amount constraint regions both are of the same dimensionality, they do not have the same configuration. Clearly, the three experimental approaches explore different subregions of the space of all mixture-amount combinations.

To investigate further the differences in the constraint regions associated with the three types of experiments, recall the earlier remark that the constraints in Table 6.1 for a particular approach impose implicit restrictions on the values of the variables used in the other approaches. For example, the component amount constraints in

Table 6.1. Usual Constraints for Mixture-Amount, Component Amount, and Component-Wise Mixture Experiments

(a) Mixture-Amount

$$0 \le L_i \le x_i \le U_i \le 1 , \quad i=1,2,\ldots,q$$

$$\sum_{i=1}^{q} x_i = 1 \qquad \text{and} \qquad A_1 \le A \le A_r .$$

(b) Component Amount

$$0 \le l_i \le a_i \le u_i , \quad i=1,2,\ldots,q.$$

(c) Component-Wise Mixture

$$0 \le l_i \le a_i \le u_i \le a_i^0 , \quad i=1,2,\ldots,q$$

$$\text{where } \sum_{i=1}^{q} (1/a_i^0)a_i = 1$$

or

$$0 \le l_i^* \le x_i^* \le u_i^* \le 1 , \quad i=1,2,\ldots,q$$

$$\text{and } \sum_{i=1}^{q} x_i^* = 1, \text{ where } x_i^* = x_i/a_i^0, \; l_i^* = l_i/a_i^0,$$

$$\text{and } u_i^* = u_i/a_i^0, \quad i=1,2,\ldots,q.$$

Table 6.1(b) impose the implicit restrictions

$$\frac{l_i}{l_i + \sum_{j\neq i}^{q} u_j} \leq x_i \leq \frac{u_i}{u_i + \sum_{j\neq i}^{q} l_j} \qquad i=1,2,\ldots,q$$

$$\sum_{j=1}^{q} l_j \leq A \leq \sum_{j=1}^{q} u_j \qquad (6.1)$$

on the component proportions and total amount of the mixture. The mixture-amount constraints in Table 6.1(a) impose the implicit restrictions

$$0 \leq L_i A_1 \leq a_i \leq U_i A_r \leq 1 , \qquad i=1,2,\ldots,q \qquad (6.2)$$

on the component amounts. These implicit restrictions define <u>implied constraint regions</u>. Let us consider some two-component examples to see how the implied constraint regions compare to the explicit constraint regions defined in Table 6.1.

Consider a component amount experiment where the two component amounts are restricted by

$$1 \leq a_1 \leq 4 \quad \text{and} \quad 2 \leq a_2 \leq 3 . \qquad (6.3)$$

The component amount constraint region defined by (6.3) is displayed as the solid rectangle in Figure 6.1. The restrictions (6.3) impose the implicit restrictions

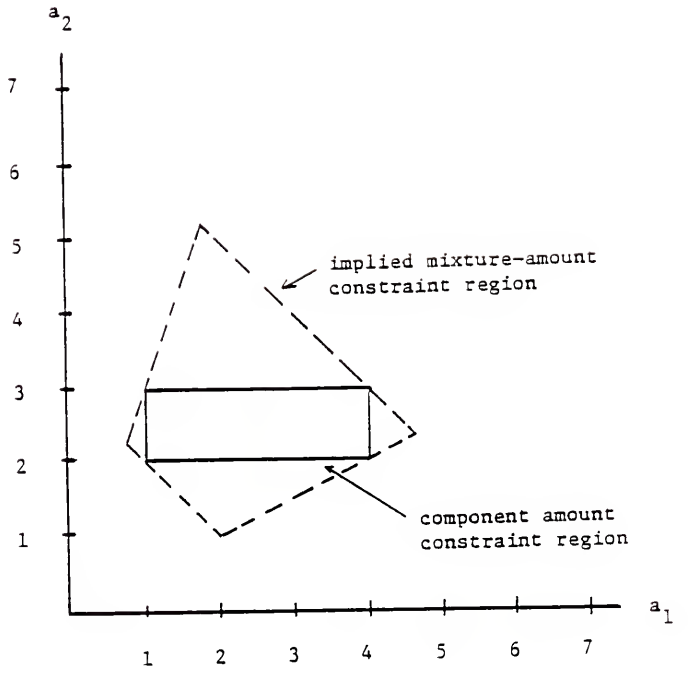


Figure 6.1. The Rectangular Constraint Region for a Component Amount Experiment and the Implied Mixture-Amount Constraint Region

$$\frac{1}{4} \leq x_1 \leq \frac{2}{3} \quad , \quad \frac{1}{3} \leq x_2 \leq \frac{3}{4} \quad , \quad 3 \leq A \leq 7 \qquad (6.4)$$

on the component proportions and the total amount. [These restrictions were obtained using formulas (6.1).] The implied mixture-amount constraint region defined by (6.4) is pictured in Figure 6.1 as the dashed region. The implied mixture-amount constraint region is circumscribed about the component amount constraint region [owing to the nature of the implicit restrictions in (6.1)]. This says that if a mixture-amount experiment is to be performed so that the ranges of the component proportions and the total amount variable are to be equivalent to those in the corresponding component amount experiment, then the constraint region of this mixture-amount experiment will be considerably larger in area or volume than the constraint region of the component amount experiment. This is because the component amount constraint region covers only small subsets of the full ranges of component proportions for any given total amount, and the subsets of the ranges covered change drastically as the total amount varies. As an illustration of this for the example pictured in Figure 6.1, note that for $A = 3.5$, the component amount constraint region covers the component proportion values $2/7 \leq x_1 \leq 3/7$ and $4/7 \leq x_2 \leq 5/7$. For $A = 6.5$, the values covered are $7/13 \leq x_1 \leq 8/13$ and $5/13 \leq x_2 \leq 6/13$. These subsets of values are only small fractions of the full ranges of the component

proportions given in (6.4). Further, the subset of the x_1 (alternately x_2) values covered by the component amount constraint region at A = 3.5 does not intersect the subset of the x_1 (alternately x_2) values covered at A = 6.5.

Now, consider a two-component mixture-amount experiment where the component proportions and total amount are constrained by

$$.2 \leq x_1 \leq .7, \quad .3 \leq x_2 \leq .8, \quad \text{and } 3 \leq A \leq 5 . \tag{6.5}$$

These restrictions impose the implicit restrictions

$$0.6 \leq a_1 \leq 3.5 \quad \text{and} \quad 0.9 \leq a_2 \leq 4.0 \tag{6.6}$$

on the component amounts [see (6.2)]. The mixture-amount constraint region defined by (6.5) and the implied component amount constraint region defined by (6.6) are both displayed in Figure 6.2. The nature of the implicit restrictions (6.6) cause the implied component amount constraint region to be circumscribed about the mixture-amount constraint region. This says that if a component amount experiment is to be performed where the ranges of the component amounts are equivalent to those in a corresponding mixture-amount experiment, then the constraint region of the component amount experiment will be considerably larger in area or volume than the constraint region of the mixture-amount experiment. This is because the mixture-amount constraint region covers, for a given amount of one of the components,

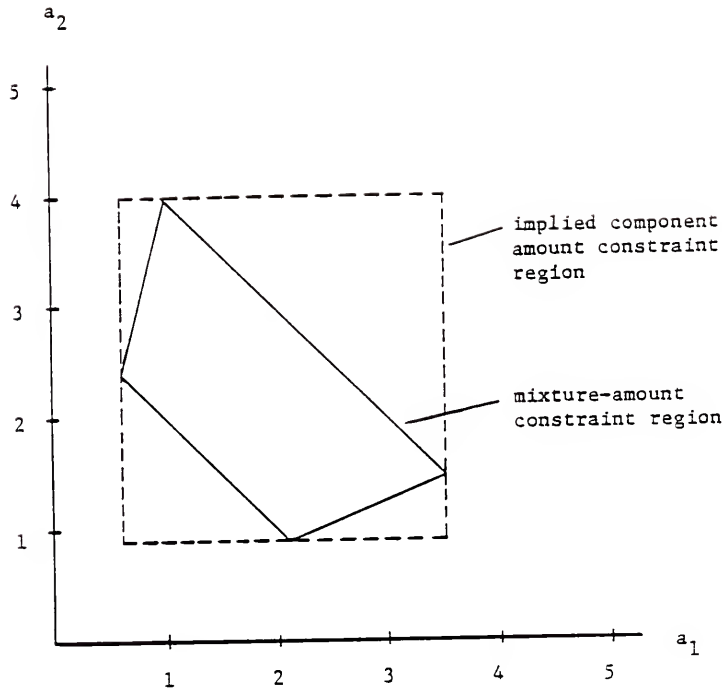


Figure 6.2. The Mixture-Amount Constraint Region and the Implied Component Amount Constraint Region

only a subset of the full range of amount values for each of the other remaining components, and the subsets of ranges covered change as the amount of the given component varies.

As a final example, consider a component-wise mixture experiment in two components with arbitrary base values $a_1^0 = 10$ and $a_2^0 = 10/3$, and restrictions

$$1 \leq a_1 \leq 4, \quad 2 \leq a_2 \leq 3, \text{ and}$$

$$(1/10)a_1 + (3/10)a_2 = 1 \ . \tag{6.7}$$

The component-wise mixture constraint region defined by (6.7) is pictured in Figure 6.3(a), and is seen to be one-dimensional. Figures 6.3(b) and 6.3(c) show the constraint region (6.7) depicted as a subspace of the corresponding implied constraint regions for a component amount and a mixture-amount experiment, respectively. The implied component amount and mixture-amount constraint regions shown in Figures 6.3(b) and 6.3(c), are respectively defined by

$$1 \leq a_1 \leq 4 \quad \text{and} \quad 2 \leq a_2 \leq 3 \tag{6.8}$$

and

$$\frac{1}{4} \leq x_1 \leq \frac{2}{3} \ , \ \frac{1}{3} \leq x_2 \leq \frac{3}{4} \ , \ 4 \leq A \leq 6 \ . \tag{6.9}$$

The first two examples above served to illustrate how the usual explicit constraints for a mixture-amount experiment impose implicit constraints on the values of the

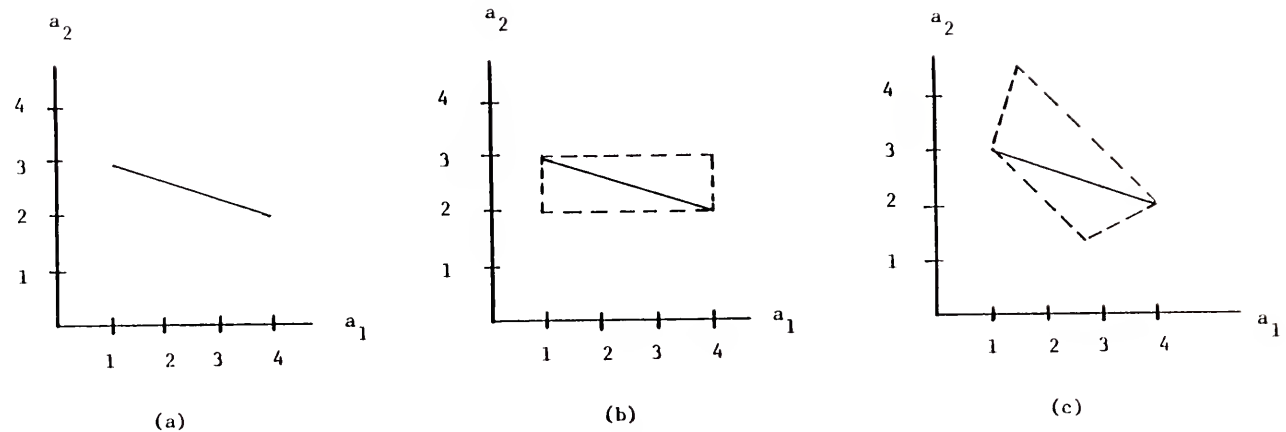


Figure 6.3. Component-Wise Mixture Constraint Region (a) and the Component-Wise Mixture Constraint Region as a Subspace of a Component Amount Constraint Region (b), and as a Subspace of a Mixture-Amount Constraint Region (c)

variables of the component amount experiment and vice versa. The implicit constraints define an implied constraint region that is circumscribed about the explicit constraint region. The third example demonstrated how the constraint region of a component-wise mixture experiment may be viewed as a subspace of dimensionality one less than the dimensionality of the implied constraint region of a mixture-amount or a component amount experiment.

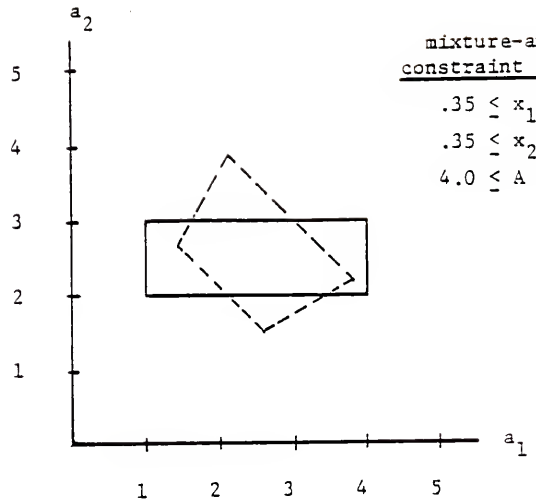
In general, the examples illustrate that an implied constraint region associated with a given type of experiment is significantly larger in area or volume than the explicit constraint region for that experiment. This is also true in the case of component-wise mixture experiments, since the explicit constraint region for such an experiment is of dimensionality one less than the dimensionality of the implied constraint region of a mixture-amount or component amount experiment. (In some sense, this is a reason why it might be said that the constraint region of a component-wise mixture experiment should not be compared to constraint regions of mixture-amount or component amount experiments.) However, constraint regions of mixture-amount and component amount experiments can be compared on an equal (same dimensionality) basis.

It is possible to construct mixture-amount and component amount constraint regions having the same centroid and equal areas or volumes. Comparing constraint regions

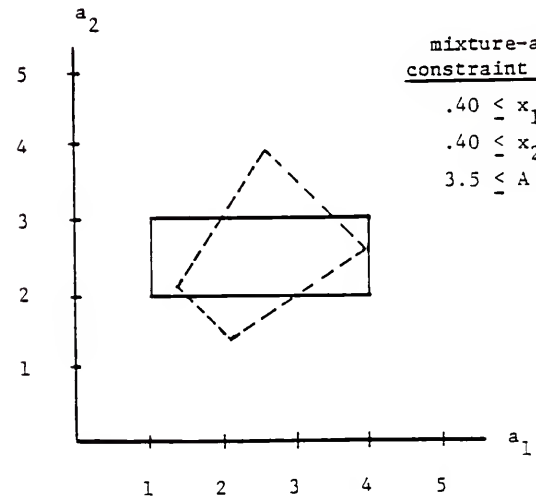
constructed in this manner allows us to focus on the portions of the mixture space contained in both constraint regions and the portions contained only in one or the other constraint region. Such a comparison is in some sense more "fair" than comparing explicit and implied constraint regions. As an example, Figure 6.4 displays two different mixture-amount constraint regions (dashed figures) having the same centroid and area as the rectangular component amount constraint region (solid figures) taken from Figure 6.1. While it is clear that there are an infinite number of such mixture-amount constraint regions, only those which overlap considerably with the rectangular component amount constraint region are of interest for our purposes. Each of the two mixture-amount constraint regions in Figure 6.4 has a considerable fraction of its area in common with the component amount constraint region [0.63 for Figure 6.4(a) and 0.62 for Figure 6.4(b)]. The mixture-amount constraint region having maximum area in common with the component amount constraint region (maximum fraction = 0.65) is given by the restrictions

$$.36 \leq x_1 \leq .64, \quad .36 \leq x_2 \leq .64, \quad 3.9 \leq A \leq 6.1 \ . \qquad (6.10)$$

Even for the "best comparison" of the component amount constraint region (6.8) and the mixture-amount constraint region (6.10), the two constraint regions only share 65% of their area. The 35% of the mixture-amount constraint region



(a)



(b)

Figure 6.4. Mixture-Amount Constraint Regions Having the Same Centroid and Area as the Rectangular Component Amount Constraint Region in Figure 6.1

not in the component amount region contains points (a_1,a_2) with both smaller and larger values of a_2 (namely $1.4 \leq a_2 \leq 3.9$) than are contained in the component amount constraint region (where $2 \leq a_2 \leq 3$). Alternately, the 35% of the component amount constraint region not in the mixture-amount region contains points $(a_1=x_1A,\ a_2=x_2A)$ with smaller and larger values of x_1, x_2, and A ($1/4 \leq x_1 \leq 2/3$, $1/3 \leq x_2 \leq 3/4$, $3 \leq A \leq 7$) than are contained in (6.10).

In summary, mixture-amount and component amount constraint regions are noticeably different in terms of configuration, orientation, and subregion of the total mixture space covered. A component-wise mixture constraint region is of dimensionality one less than, and may be thought as a subspace of, a mixture-amount or component amount constraint region.

6.2 Comparison of Models

In this section, we continue the comparison of mixture-amount, component amount, and component-wise mixture experiments by concentrating on the model forms used with each approach. (The model forms associated with these types of experiments were discussed in Chapters 3 and 5.) Recalling the definition of a general mixture experiment (Section 1.3), it is the form of the model that distinguishes the particular type of general mixture experiment. Hence, comparing the model forms used with each approach sheds

light on the similarities and differences of the three types of general mixture experiments under consideration.

It was noted in the previous section that the dimensionality of the constraint region of a component-wise mixture experiment is one less than the dimensionality of the constraint region of a mixture-amount or a component amount experiment. Hence, the response surface to be approximated in a component-wise mixture experiment is also of dimensionality one less than that of the surface of a mixture-amount or component amount experiment (with the same number of components). Thus, from a modeling viewpoint, the component-wise mixture approach is not directly comparable to a mixture-amount or a component amount approach. With this in mind, we will compare only mixture-amount and component amount models in this section. Before doing so however, let us briefly discuss component-wise mixture models.

Two basic model forms for component-wise mixture experiments were discussed in Section 5.2; one in terms of component amounts and the other in terms of component-wise proportions. Both basic model forms are analogous to the usual mixture models and are appropriate when the total amount of the mixture (which varies in this type of experiment) affects the response. If the total amount does not affect the response (even though it is not fixed in an experiment of this type), the usual mixture models are appropriate for modeling the response data. Unfortunately,

the component-wise mixture designs do not provide any way to test whether or not the total amount of the mixture affects the response (see Section 6.3 for more discussion of this point).

We now turn to the comparison of mixture-amount and component amount models. Models for mixture-amount or component amount analyses are directly comparable, since models of either type can be used to fit a given set of data generated by a (q+1)-dimensional response surface. Having two potential model types opens the door to questions of comparison. Does it matter which type is used? If so, is one type clearly preferable or is each type preferable for certain kinds of problems? While these questions nominally involve the comparison of model types, they also involve the comparison of the mixture-amount and component amount experimental approaches as a whole. That is, if one of the model types turns out to be clearly superior to the other for certain kinds of problems, that particular model type and its corresponding design would be chosen over the other.

We begin by comparing the two model types from a pre-experiment viewpoint. That is, before beginning an experiment one must decide whether to use a mixture-amount or a component amount experimental approach. Comparing the models associated with these approaches may provide us with some input as to which approach should be chosen. There are two main viewpoints from which to compare the two model

types. The first is the interpretative value of the model forms, i.e., what interpretations do the parameters in the model have? The second is the predictive ability of the models, i.e., how well does each model form explain different kinds of response behavior? In comparing the two model types, we shall first consider the interpretative value of the model forms.

Let us assume an experimenter is interested in estimating the blending properties of the mixture components and in determining if and how varying the total amount affects these properties. Recall from Chapter 3 that a mixture-amount model of the form (3.5) [or one based on other forms of η_C or $\beta_m(A)$] contains terms that represent the linear and nonlinear blending properties of the components at the average level of amount when the coded levels of amount have mean zero (or averaged over all levels of amount when orthogonal polynomial coding is used). The remaining terms in the mixture-amount model explain how varying the amount of the mixture affects the blending properties of the components. Hence the mixture-amount models <u>separate</u> the component blending information and the amount effect information. On the other hand, the component amount models (4.1) and (4.2) do not separate the component blending and amount effect information, since their terms involve the $a_i = x_i A$, $i=1,2, \ldots ,q$ (where A is the uncoded total amount variable). Hence, if the experimenter is interested in

investigating the component blending properties and how varying the amount of the mixture affects the component blending, then the mixture-amount models are preferred from the model interpretation viewpoint. However, if the experimenter is not interested in this blending information, but only wants to know the amount of each component needed to obtain the optimum response, then the component amount models would suffice.

Let us now turn our attention to predictive ability in comparing the two model types. We would like to know if both model types are equivalent in their ability to describe different kinds of response behavior, or if one or the other of the model types is potentially superior for fitting certain kinds of response surfaces. It is informative to take a mixture-amount model and write it in terms of the component amount variables.

Consider the linear by linear mixture-amount model

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_i^1 x_i A \ , \qquad (6.11)$$

where A is uncoded. Replacing $\beta_q^0 x_q$ in (6.11) with $\beta_q^0(1 - \sum_{i=1}^{q-1} x_i)$ and then reexpressing x_i as a_i/A yields

$$\eta = \beta_q^0 + \sum_{i=1}^{q-1}(\beta_i^0 - \beta_q^0)x_i + \sum_{i=1}^{q}\beta_i^1 x_i A$$

$$= \alpha_0 + \sum_{i=1}^{q}\alpha_i a_i + \sum_{i=1}^{q-1}(\beta_i^0 - \beta_q^0)(a_i/A) \ , \qquad (6.12)$$

where $\alpha_0 = \beta_q^0$ and $\alpha_i = \beta_i^1$, i=1,2, . . . ,q. Hence, we see from (6.12) that (6.11) can be viewed as an expanded model form of the first-degree component amount model (5.1). The extra terms in (6.12) not found in (5.1) involve a_i/A.

Now, consider the quadratic by quadratic mixture-amount model

$$\eta = \sum_{i=1}^{q}\beta_i^0 x_i + \sum_{i<j}^{q}\sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q}\beta_i^1 x_i A + \sum_{i<j}^{q}\sum \beta_{ij}^1 x_i x_j A$$

$$+ \sum_{i=1}^{q}\beta_i^2 x_i A^2 + \sum_{i<j}^{q}\sum \beta_{ij}^2 x_i x_j A^2 \ , \qquad (6.13)$$

where A is uncoded. Rewriting (6.13) in terms of the a_i yields (see Appendix E)

$$\eta = \alpha_0 + \sum_{i=1}^{q}\alpha_i a_i + \sum_{i=1}^{q}\alpha_{ii} a_i^2 + \sum_{i<j}^{q}\sum \alpha_{ij} a_i a_j$$

$$+ \sum_{i=1}^{q-1}(\beta_i^0 - \beta_q^0)(a_i/A) + \sum_{i<j}^{q}\sum \beta_{ij}^1 (a_i a_j/A)$$

$$+ \sum_{i<j}^{q}\sum \beta_{ij}^0 (a_i a_j/A^2) \ , \qquad (6.14)$$

where $\alpha_0 = \beta_q^0$, $\alpha_i = \beta_i^1$, $\alpha_{ii} = \beta_i^2$, i=1,2, . . . ,q and $\alpha_{ij} = \beta_i^2 + \beta_j^2 + \beta_{ij}^2$, all i < j. This shows that (6.14) [and hence (6.13)] is an expanded form of the second-degree component amount model (5.2). The extra terms in (6.14) not found in (5.2) involve a_i/A, $a_i a_j/A$, and $a_i a_j/A^2$.

Let us briefly review what we have learned so far about the predictive ability of the two model types. By rewriting the canonical polynomial mixture-amount models in terms of the a_i, the resulting models (and hence the equivalent mixture-amount models) are seen to be expanded forms of polynomial component amount models. Moreover, the "extra" terms in the rewritten mixture-amount models are not polynomial functions of the a_i. The following example illustrates the possible importance of the extra terms in a mixture-amount model that are not contained in the corresponding polynomial component amount model.

Consider a simple hypothetical situation with two mixture components and two total amounts ($A_1 < A_2$). We assume the components blend linearly at both total amounts:

$$\eta_{A_1} = ax_1 + bx_2$$

$$\eta_{A_2} = cx_1 + dx_2 \,. \qquad (6.15)$$

It is shown in Appendix F that a mixture-amount model of the form

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_1^1 x_1 A + \beta_2^1 x_2 A \qquad (6.16)$$

exactly fits the situation described by (6.15), where

$$\beta_1^0 = \frac{aA_2 - cA_1}{A_2 - A_1} \qquad \beta_2^0 = \frac{bA_2 - dA_1}{A_2 - A_1}$$

$$\beta_1^1 = \frac{c - a}{A_2 - A_1} \qquad \beta_2^1 = \frac{d - b}{A_2 - A_1} \; . \qquad (6.17)$$

These parameters are interpreted as follows:

β_i^0 = the difference in the expected responses to component i weighted by the levels of A, relative to the difference in the levels of A,

β_i^1 = the difference in the expected responses to component i at the two levels of A, relative to the change in the levels of A.

Note that these interpretations reduce to the usual interpretations given in Chapter 3 when A_1 and A_2 are replaced by the coded values -1 and +1. However, for comparison purposes, we retain the uncoded form of the total amount variable.

We want to know how well the first-degree component amount model

$$\eta = \alpha_0 + \alpha_1 a_1 + \alpha_2 a_2 \; , \qquad (6.18)$$

which has one less term than (6.16), fits the situation described by (6.15). Recall that (6.18) is a reduced form

of (6.16) if $\beta_1^0 = \beta_2^0$, which by (6.17), is equivalent to

$$d - c = (A_2/A_1)(b - a) . \tag{6.19}$$

The differences (b-a) and (d-c) are the slopes of the lines in (6.15) defined when changing the blends from (1,0) to (0,1). These slopes measure the effect of increasing the proportion x_2 at the total amounts A_1 and A_2, respectively. Hence, (6.19) implies that the component amount model (6.18) is appropriate for the situation described by (6.15) only if the effect of increasing x_2 at amount A_2 is (A_2/A_1) times the effect of increasing x_2 at amount A_1. This is a very restrictive assumption and indicates that the component amount model (6.18) could give a poor fit for some situations.

So far in this section, we have been comparing polynomial component amount models to mixture-amount models where in the latter model forms η_C is a Scheffé canonical polynomial and the $\beta_m(A)$ are defined using a polynomial in A. However, recall that we have the flexibility to choose other than canonical polynomials for η_C and other than polynomial expressions for $\beta_m(A)$ when forming mixture-amount models. In general, any mixture-amount model can be rewritten in terms of the component amount variables, with the resulting expression a nonpolynomial function of the a_i's. Hence, the ability of polynomial component amount models to

approximate the behavior of response surfaces where such mixture-amount models are appropriate is questionable.

An obvious alternative to polynomial component amount models would be to consider nonpolynomial models in the a_i. A component amount model equivalent to any mixture-amount model could be developed by reexpressing x_i as a_i/A in the mixture-amount model (as done earlier in this section). Depending on the mixture-amount model under consideration, the resulting component amount model may involve complicated functions of the a_i and hence be of little interpretative value. Also, unless we augment or modify the resulting component amount model, we might as well use the model in its mixture-amount form.

To summarize, we have noted that mixture-amount models provide information about the "average" component blending properties and how changing the amount of the mixture affects these blending properties. Component amount models do not separate these two types of information. This important difference between the two types of models is a good reason for prefering the mixture-amount experimental approach over the component amount approach. We also noted that any mixture-amount model can be rewritten in terms of the component amount variables, where the resulting expression is (in general) a nonpolynomial function of the component amounts. Hence, the predictive ability of polynomial

component amount models relative to mixture-amount models is questioned. These concerns are addressed in Section 6.4.

6.3 Comparison of Designs

In this section, we continue the comparison of mixture-amount, component amount, and component-wise mixture experiments by concentrating on the designs used with each approach. These designs were discussed in Chapters 4 and 5.

It was mentioned in Section 6.1 that the constraint region of a component-wise mixture experiment is of dimensionality one less than the dimensionality of the constraint region of a mixture-amount or component amount experiment. Hence, component-wise mixture designs are not of the same dimensionality as mixture-amount or component amount designs, and thus are not directly comparable to such designs. With this in mind, we compare only mixture-amount and component amount designs in this section. However, before we do so, let us consider very briefly component-wise mixture designs.

We mentioned in Section 5.2 that the usual mixture designs can be adapted for use in component-wise mixture experiments, where the component proportions are replaced by the component-wise proportions. A component-wise mixture design is used when there is a linear constraint on the values of the component amount variables (see Section 5.2 for examples of how a constraint of this type occurs), and

it is assumed that the response value may vary as the total amount of the mixture varies. Unfortunately, the component-wise mixture designs do not provide any clear method for testing whether or not the total amount of the mixture affects the response, or if the relative proportions of the components are affecting the response. This is because the component blending information is completely confounded with the information about the effect of total amount on component blending. If tests of these separate effects are desired and the linear constraint on the component amounts can be relaxed enough to allow mixtures of the components to be conducted at the same amount, a mixture-amount approach could be used. The ability to investigate the effect of total amount on the response is gained at the expense of increasing the dimensionality of the constraint region by one.

We now turn to the comparison of mixture-amount and component amount designs. Designs corresponding to the mixture-amount and component amount approaches are directly comparable since the constraint regions for each are q-dimensional (for q components).

The component amount designs mentioned in Section 5.1 include factorial, fractional factorial, and central composite designs. The mixture-amount designs discussed in Chapter 4 include complete and fractional versions of simplex-lattice, simplex-centroid, radial, axial, inverse

term, ratio, log-ratio, and extreme vertices based designs. Obviously, we cannot compare all of these types of mixture-amount designs to the several types of component amount designs. However, without performing any comparisons, it should be clear that component amount designs are best for component amount models and mixture-amount designs are best for mixture-amount models.

Our interest in comparing mixture-amount and component amount designs is to see how much support one type of design provides for a model of the other type. For example, we noted in the previous section that mixture-amount models provide more interpretative information in that they separate the "average" component blending properties from the effect of the total amount on component blending. Now, suppose that data from a component amount design is available. What kind of support does this component amount design provide for fitting a mixture-amount model? Similarly, we want to know what kind of support a mixture-amount design provides for fitting a component amount model.

It is reasonable to anticipate possible multicollinearity problems when fitting one type of model (mixture-amount or component amount) to data collected from a design of the other type, due to the differences in configuration and orientation of the two types of constraint regions (see Section 6.1). When the multicollinearity problems are

severe, the variances of some (or possibly all) of the parameter estimates may be very inflated. In such a case, it might be of little value to fit a mixture-amount model to data from a component amount design (or vice versa).

To investigate the above questions and concerns, let us return to the two-component example introduced in Section 6.1. Previously in that section, we compared the mixture-amount constraint region (6.10) to the component amount constraint region (6.8), and noticed that these two constraint regions had the maximum common area among pairs of constraint regions with the same centroid and the same area. The two constraint regions were chosen in this way to allow for as fair a comparison as possible. A fair comparison of designs for this example is achieved by choosing designs which cover the constraint regions (6.8) and (6.10). Listed in Table 6.2 and pictured in Figure 6.5 are a nine-point (3^2) component amount design and a nine-point constrained mixture-amount design. These two designs will be compared with respect to the multicollinearity they exhibit when used in fitting each of the four mixture-amount models and each of the four component amount models shown in Table 6.3. In Table 6.3, the primes on x_1, x_2, A, a_1, and a_2 denote coded forms of these variables. The codings for A', a_1', and a_2' for both designs in Table 6.2 are given by

Table 6.2. Mixture-Amount and Component Amount Designs for a Two-Component Example

	Mixture-Amount Design						Corresponding Component Amount Values			
Pt	x_1	x_2	A	x_1'	x_2'	A'	a_1	a_2	a_1'	a_2'
1	.36	.64	3.9	0.0	1.0	-1	1.404	2.496	-.7307	-0.0080
2	.50	.50	3.9	0.5	0.5	-1	1.950	1.950	-.3667	-1.1000
3	.64	.36	3.9	1.0	0.0	-1	2.496	1.404	-.0027	-2.1920
4	.36	.64	5.0	0.0	1.0	0	1.800	3.200	-.4667	1.4000
5	.50	.50	5.0	0.5	0.5	0	2.500	2.500	.0000	0.0000
6	.64	.36	5.0	1.0	0.0	0	3.200	1.800	.4667	-1.4000
7	.36	.64	6.1	0.0	1.0	+1	2.196	3.904	-.2027	2.8080
8	.50	.50	6.1	0.5	0.5	+1	3.050	3.050	.3667	1.1000
9	.64	.36	6.1	1.0	0.0	+1	3.904	2.196	.9360	-0.6080

	Component Amount Design				Corresponding Mixture-Amount Values					
Pt	a_1	a_2	a_1'	a_2'	x_1	x_2	A	x_1'	x_2'	A'
1	1.0	2.0	-1	-1	1/3	2/3	3.0	0.2000	0.8000	-1.8181
2	1.0	2.5	-1	0	2/7	5/7	3.5	0.0857	0.9143	-1.3636
3	1.0	3.0	-1	+1	1/4	3/4	4.0	0.0000	1.0000	-0.9091
4	2.5	2.0	0	-1	5/9	4/9	4.5	0.7333	0.2667	-0.4545
5	2.5	2.5	0	0	1/2	1/2	5.0	0.6000	0.4000	0.0000
6	2.5	3.0	0	+1	5/11	6/11	5.5	0.4909	0.5091	0.4545
7	4.0	2.0	+1	-1	2/3	1/3	6.0	1.0000	0.0000	0.9091
8	4.0	2.5	+1	0	8/13	5/13	6.5	0.8769	0.1231	1.3636
9	4.0	3.0	+1	+1	4/7	3/7	7.0	0.7714	0.2286	1.8181

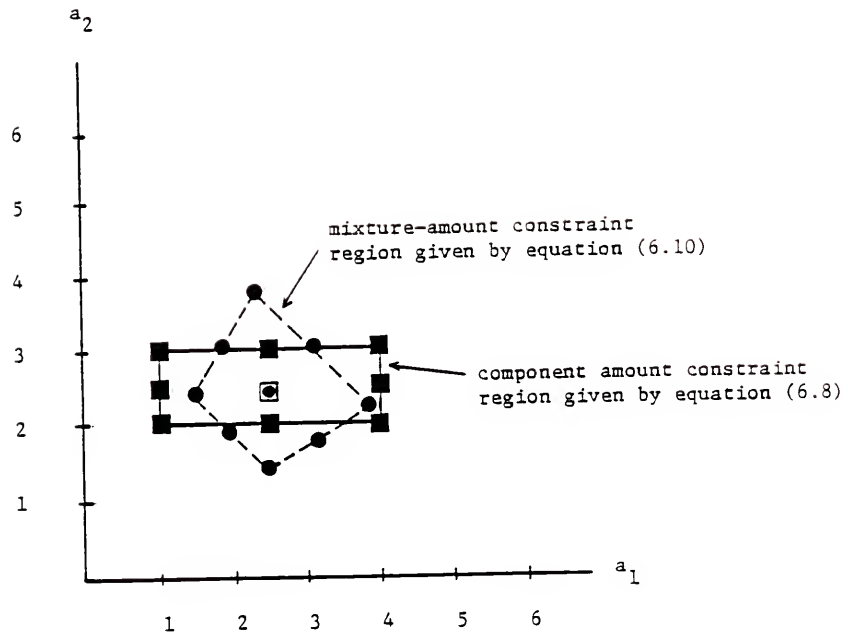


Figure 6.5. Mixture-Amount and Component Amount Designs for a Two-Component Example

Table 6.3. Two-Component Mixture-Amount and Component Amount Models for Comparing the Two Designs in Table 6.2

Mixture-Amount Models

1. $\eta = \beta_1^0 x_1' + \beta_2^0 x_2' + \beta_{12}^0 x_1' x_2' + \beta_0^1 A'$

2. $\eta = \beta_1^0 x_1' + \beta_2^0 x_2' + \beta_{12}^0 x_1' x_2' + \beta_1^1 x_1' A' + \beta_2^1 x_2' A'$

3. $\eta = \beta_1^0 x_1' + \beta_2^0 x_2' + \beta_{12}^0 x_1' x_2' + \beta_1^1 x_1' A' + \beta_2^1 x_2' A' + \beta_{12}^1 x_1' x_2' A'$

4. $\eta = \sum_{h=0}^{2} [\beta_1^h x_1' + \beta_2^h x_2' + \beta_{12}^h x_1' x_2'](A')^h$

Component Amount Models

5. $\eta = \alpha_0 + \alpha_1 a_1' + \alpha_2 a_2'$

6. $\eta = \alpha_0 + \alpha_1 a_1' + \alpha_2 a_2' + \alpha_{12} a_1' a_2'$

7. $\eta = \alpha_0 + \alpha_1 a_1' + \alpha_2 a_2' + \alpha_{12} a_1' a_2' + \alpha_{11}(a_1')^2 + \alpha_{22}(a_2')^2$

8. $\eta = \alpha_0 + \alpha_1 a_1' + \alpha_2 a_2' + \alpha_{12} a_1' a_2' + \alpha_{11}(a_1')^2 + \alpha_{22}(a_2')^2$
$+ \alpha_{112}(a_1')^2 a_2' + \alpha_{122} a_1'(a_2')^2 + \alpha_{1122}(a_1')^2 (a_2')^2$

$$A' = \frac{A - 5}{1.1} \tag{6.20}$$

$$a_1' = \frac{a_1 - 2.5}{1.5} \qquad a_2' = \frac{a_2 - 2.5}{0.5} . \tag{6.21}$$

The codings for x_1' and x_2' with the mixture-amount design are

$$x_1' = \frac{x_1 - .36}{.28} \qquad x_2' = \frac{x_2 - .36}{.28} , \tag{6.22}$$

and for the component amount design are

$$x_1' = \frac{x_1 - 1/4}{5/12} \qquad x_2' = \frac{x_2 - 1/3}{5/12} . \tag{6.23}$$

The codings given in (6.22) and (6.23) are just the respective L-pseudocomponent transformations [see equation (1.13) in Chapter 1] for each design.

As indicators of the degree of multicollinearity, we utilize the variance inflation factors (VIF's) associated with the parameter estimates and the condition number (CN) of the design. The VIF's and the CN are model dependent as well as design dependent, and also depend on the coding of the terms in the model. As a first step in computing (and defining) the VIF's and the CN, the columns of the expanded design matrix (which correspond to the terms in the model under consideration) are standardized. For component amount models, the model terms (excluding the intercept term) are standardized as

$$w_{ij} = \frac{z_{ij} - \bar{z}_{\cdot j}}{\sqrt{\sum_{h=1}^{N} (z_{hj} - \bar{z}_{\cdot j})^2}} \qquad i=1,\ldots,N;\ j=1,\ldots,p, \qquad (6.24)$$

where z_{ij} is the value of the jth term in the model for the ith observation, and p is the number of terms (not counting the intercept term) in the associated component amount model. As an example, the z variables for model 7 in Table 6.3 are $z_{i1} = a'_{i1}$, $z_{i2} = a'_{i2}$, $z_{i3} = a'_{i1}a'_{i2}$, $z_{i4} = (a'_{i1})^2$, and $z_{i5} = (a'_{i2})^2$, where i=1,2, . . . ,N. For this example, p = 5.

For mixture-amount models, the model terms are standardized as

$$w_{ij} = \frac{z_{ij}}{\sqrt{\sum_{h=1}^{N} z_{hj}^2}} \qquad i=1,\ldots,N;\ j=1,\ldots,p\ , \qquad (6.25)$$

where z_{ij} is the value of the jth term in the model for the ith observation, and p is the number of terms in the associated mixture-amount model. As an example, the z variables for model 1 in Table 6.3 are $z_{i1} = x'_{i1}$, $z_{i2} = x'_{i2}$, $z_{i3} = x'_{i1}x'_{i2}$, and $z_{i4} = A'$. For this example, p = 4.

Now, for mixture-amount or component amount models, let $W = (\underline{w}_1, \ldots, \underline{w}_j, \ldots, \underline{w}_p)$ where $\underline{w}_j = (w_{ij}, \ldots, w_{Nj})'$, with the w_{ij} coming from (6.24) or (6.25). Then the VIF's are the diagonal elements of $(W'W)^{-1}$.

Marquardt (1970) remarked that if any of the VIF's are greater than 10, the corresponding least squares parameter estimates may be so poorly estimated that they are of little interpretative value. Gorman's (1970) findings, on the other hand, suggest that VIF's over 100 should serve as a warning of possible numerical accuracy problems (especially if the least squares estimation is conducted using single precision computer routines). For further discussion of VIF's and multicollinearity in general, see (in addition to the articles referenced above) St. John (1984), Montgomery and Peck (1982), and Gunst and Mason (1980).

The condition number CN of the matrix $W'W$ is defined as the ratio

$$CN = \lambda_p/\lambda_1 , \qquad (6.26)$$

where $\lambda_1 \leq \lambda_2 \leq \ldots \leq \lambda_p$ are the p eigenvalues of $W'W$. Condition numbers between 100 and 1000 imply moderate to strong multicollinearity, while a value over 1000 indicates severe multicollinearity (Montgomery and Peck 1982).

The VIF's and CN's computed based on the designs in Table 6.2 are given in Tables 6.4 and 6.5 for the mixture-amount and component amount models in Table 6.3. The values $\det(W'W)$ are also given in Tables 6.4 and 6.5. Montgomery and Peck note that, in general, $0 \leq \det(W'W) \leq 1$ and state that "$100[\det(W'W)^{-1/2} - 1]$ reflects the percentage increase

Table 6.4. VIF's, CN's, and det(W'W)'s for the Four Mixture-Amount Models in Table 6.3 Using the Mixture-Amount and Component Amount Designs of Table 6.2

	Variance Inflation Factors							
	Model 1		Model 2		Model 3		Model 4	
Par.	MA Design	CA Design	MA Design	CA Design	MA Design	CA Design	MA Design	CA Design
β_1^0	1.25	3.96	1.25	6.13	1.25	19.10	3.75	110.38
β_2^0	1.25	3.27	1.25	9.20	1.25	41.21	3.75	248.18
β_{12}^0	1.50	3.38	1.50	6.24	1.50	6.24	4.50	47.39
β_1^1			1.04	3.80	1.25	30.12	1.25	129.74
β_2^1			1.04	6.72	1.25	66.19	1.25	1208.01
β_{12}^1					1.50	48.21	1.50	233.41
β_1^2							3.75	766.39
β_2^2							3.75	800.21
β_{12}^2							4.50	687.63
β_0^1	1.00	2.98						
CN	3.79	15.83	3.79	56.27	3.79	491.08	37.48	16043.7
det(W'W)	6.4-01	8.6-02	6.1-01	1.4-02	4.1-01	3.0-04	9.7-03	1.5-10*

* The notation 1.5-10 denotes the number 1.5×10^{-10}.

Table 6.5. VIF's, CN's, and det(W'W)'s for the Four Component Amount Models in Table 6.3 Using the Mixture-Amount and Component Amount Designs of Table 6.2

	Variance Inflation Factors							
	Model 5		Model 6		Model 7		Model 8	
Par.	MA Design	CA Design	MA Design	CA Design	MA Design	CA Design	MA Design	CA Design
α_0	--	--	--	--	--	--	--	--
α_1	1.07	1.00	1.18	1.00	1.26	1.00	3.92	3.00
α_2	1.07	1.00	1.18	1.00	1.26	1.00	3.92	3.00
α_{12}			1.17	1.00	1.59	1.00	2.83	1.00
α_{11}					1.87	1.00	3.11	3.00
α_{22}					1.87	1.00	3.11	3.00
α_{112}							5.37	3.00
α_{122}							5.37	3.00
α_{1122}							2.68	5.00
CN	1.7	1.0	2.4	1.0	6.7	1.0	41.47	17.9
det(W'W)	.94	1.0	.80	1.0	.35	1.0	4.8-03	2.2-02*

* The notation 2.2-02 denotes the number 2.2×10^{-2}.

in the volume of the joint confidence region for $\underline{\beta}$ because of the near linear dependencies in W" (1982, pg. 305).

In viewing the values of the VIF's, CN's, and $\det(W'W)$'s in Tables 6.4 and 6.5, it is clear that multicollinearity does exist for our example when fitting one type of model (mixture-amount or component amount) to a design of the other type. In Table 6.4, it is seen that the multicollinearity problems increase as the mixture-amount models become more sophisticated. While the same comment holds true for the component amount models in Table 6.5, the multicollinearity problems related to fitting component amount models to the mixture-amount design in our example do not appear to be as severe as when fitting the mixture-amount models to component amount designs. A possible reason for this is that the mixture-amount design in this example (see Figure 6.5) is similar to a central composite design, which would provide good support for fitting a component amount model. However, depending on the shape and location of the rectangular component amount constraint region, this similarity to a central composite design may be stronger or weaker for other problems.

Although we have only looked at one example, it is clear from this example and the geometry of the two types of constraint regions that multicollinearity can be a problem when fitting one type of model (mixture-amount or component amount) to a design of the other type. The problem of

multicollinearity appears to be more severe when fitting mixture-amount models to component amount designs. Also, the degree of multicollinearity increases (for both types of models) as the models to be fitted become more sophisticated. These findings suggest, for the most part, that one should fit a model corresponding to the type of design used. Although we found that multicollinearity problems were not too bad when fitting component amount models to mixture-amount designs, there is no interpretative advantage to doing so. However, as noted earlier there are times, when for interpretative reasons, we may want to fit a mixture-amount model even when the data is from a component amount design. Our findings suggest that some information about the component blending properties and how the total amount affects these blending properties can be obtained by fitting mixture-amount models to a component amount design. However, this information should be considered with caution, and care should be taken not to attach too much meaning to the estimated parameters.

6.4 Comparing the Predictive Ability of Mixture-Amount and Component Amount Models

In Section 6.2, we noted that mixture-amount models derived from the canonical polynomials are expanded forms of polynomial component amount models, where the extra terms are nonpolynomial functions of the component amounts. In general, any mixture-amount model may be written in terms of

the component amount variables, but the resulting model is usually not a polynomial function of the component amounts. This leads us to wonder whether the mixture-amount models provide a better fit for certain response surfaces than do the polynomial component amount models. We would like to investigate this hypothesis with several real data sets, but for a fair comparison of the two modeling approaches we would need data collected on both types of designs. With data from only one type of design, a fair comparison may not be possible because of potential multicollinearity problems as well as other problems related to using a nonoptimal design to fit a particular type of model.

To circumvent the above problems, we will generate "observations" at the points of a component amount design using various hypothetical "true" mixture-amount surfaces. Component amount models are then fitted to the data to see how well they approximate the mixture-amount surfaces.

For the first series of examples, we utilize the factorial component amount design that was introduced previously in Table 6.2. Observations were generated for the nine points of this design using the hypothetical "true" mixture-amount surfaces listed in Table 6.6. These six surfaces, denoted by S1, S2, . . . , S6, were chosen as being representative of several kinds of mixture-amount response behavior. A short description of each surface is given in Table 6.6.

Table 6.6. Six Hypothetical "True" Mixture-Amount Response Surfaces

S1. $\eta = 7x_1 + 6x_2 + 5A'$ *

The total amount does not affect component blending. The magnitude of the effect of total amount on the response is large relative to the component blending effects (the effect of component i is $\beta_i^0 - \beta_j^0$).

S2. $\eta = 1.5x_1 + 7.5x_2 + 0.5A'$

The total amount does not affect component blending. The magnitude of the effect of total amount on the response is small relative to the component blending effects.

S3. $\eta = 4x_1 + 5x_2 + 3x_1A' - 2x_2A'$

The components blend linearly, with total amount having a linear effect on the component blending properties.

S4. $\eta = 1x_1 + 2x_2 - 8x_1x_2 + 9x_1x_2A' - 1x_1x_2(A')^2$

The components blend linearly for $A' = +1$, with an increasing degree of nonlinear blending as the value of A' decreases.

S5. $\eta = 1.5x_1 + 2x_2 + 0.5x_1^{-1} + 0.5x_1A' - 1x_2A' + 0.5x_1^{-1}A'$

The components blend linearly for $A' = -1$, with an increasing degree of nonlinear blending (inverse term in x_1) as the value of A' increases. Note that the coefficients of the $(1/x_1)$ and $(1/x_1)A'$ terms are equal (to 0.5).

S6. $\eta = 4x_1 + 5x_2 + 3x_1A' - 2x_2A' + 2x_1(A')^2 + 1x_2(A')^2$

The components blend linearly, with total amount having a quadratic effect on the component blending properties.

---

* Note that $A' = (A - 5)/2$ above.

For each surface in Table 6.6, the first and second-degree polynomial component amount models

$$\eta = \alpha_0 + \alpha_1 a_1' + \alpha_2 a_2' \tag{6.27}$$

$$\eta = \alpha_0 + \alpha_1 a_1' + \alpha_2 a_2' + \alpha_{12} a_1' a_2' + \alpha_{11}(a_1')^2 + \alpha_{22}(a_2')^2 \tag{6.28}$$

were fitted. The primes on the a_i indicate coded forms of these variables, given by $a_1' = (a_1 - 2.5)/1.5$ and $a_2' = (a_2 - 2.5)/0.5$. As indicators of how well these two component amount models approximate the six mixture-amount response surfaces, R^2 values for each model are presented in Table 6.7. Also, a final model was obtained for each surface. This final model always contains the α_0, $\alpha_1 a_1'$, and $\alpha_2 a_2'$ terms and whichever of the $\alpha_{12} a_1' a_2'$, $\alpha_{11}(a_1')^2$, and $\alpha_{22}(a_2')^2$ terms that are significant. These final fitted models as well as their R^2 values are also presented in Table 6.7.

It is seen from the R^2 statistics in Table 6.7 that second-degree polynomial component amount models approximate the six mixture-amount surfaces very well. However, the fitted final component amount models in Table 6.7 do little to indicate the nature of the component blending or how the total amount affects the component blending.

We now consider a set of examples with three components, and utilize the central composite component amount

Table 6.7. R^2 Values and Final Fitted Component Amount Models for the "True" Surfaces from Table 6.6

Surface	R^2 Values for 1st Degree CA Model	2nd Degree CA Model	Final* CA Model
S1	0.99995	≈ 1.00	≈ 1.00
S2	0.94638	0.99950	0.99861
S3	0.10435	0.99156	0.97682
S4	0.97591	0.99943	0.99934
S5	0.91758	0.99790	0.99749
S6	0.03769	0.99958	0.99933

Surface	Final* CA Models
S1	$\hat{y} = 6.50 + 3.91a_1' + 1.20a_2' - 0.05(a_1')^2$
S2	$\hat{y} = 4.48 - 0.61a_1' + 0.40a_2' + 0.30(a_1')^2$
S3	$\hat{y} = 4.45 + 0.04a_1' + 0.13a_2' + 0.67(a_1')^2$
S4	$\hat{y} = -0.50 + 1.21a_1' + 0.64a_2' - 0.19a_1'a_2' + 0.25(a_1')^2$
S5	$\hat{y} = 2.75 + 0.15a_1' + 0.34a_2' - 0.08a_1'a_2' + 0.15(a_1')^2$
S6	$\hat{y} = 4.52 + 0.12a_1' + 0.15a_2' + 0.58a_1'a_2' + 1.48(a_1')^2$

* Final models always contain the terms α_0, $\alpha_1 a_1'$, and $\alpha_2 a_2'$, and any of the terms $\alpha_{12} a_1' a_2'$, $\alpha_{11}(a_1')^2$, $\alpha_{22}(a_2')^2$ which are significant.

design with a single center point observation listed in Table 6.8. Observations were generated at the points of this design with the surfaces defined by

$$\eta = 50x_1 + 85x_2 + 20x_3 - 125x_1x_2/(x_1+x_2) + 5A' \qquad (6.29)$$

$$\eta = 50x_1 + 85x_2 + 20x_3 - 125x_1x_2/(x_1+x_2) + 10x_1A' - 18x_2A' + 5x_3A' + 25[x_1x_2/(x_1+x_2)]A' , \qquad (6.30)$$

where $A' = (A - 9)/3$. These surfaces are of interest because they reflect an additive blending property of the third component and we want to know how well polynomial component amount models can approximate these surfaces. The R^2 values for the fitted first-degree, second-degree, and final polynomial component amount models for each of the two surfaces are given in Table 6.9. The final fitted component amount models are also given in Table 6.9.

As seen from the R^2 values in Table 6.9, the second-degree polynomial component amount models approximate the mixture-amount surfaces (6.29) and (6.30) (where one of the components blends additively) quite well. The final fitted model for the surface (6.29) does not contain the $\alpha_{13}a_1'a_3'$, $\alpha_{23}a_2'a_3'$, or $\alpha_{33}(a_3')^2$ terms, and thus seems to suggest that the third component blends additively. However, the final fitted component amount model for the surface (6.30) does contain the $\alpha_{13}a_1'a_3'$ and $\alpha_{23}a_2'a_3'$ terms, even though the third component blends additively for this surface also. Thus, in

Table 6.8. Central Composite Component Amount Design in Three Variables

a_1	a_2	a_3	a_1'	a_2'	a_3'
2.0	2.0	2.0	-1.0	-1.0	-1.0
2.0	2.0	4.0	-1.0	-1.0	1.0
2.0	4.0	2.0	-1.0	1.0	-1.0
2.0	4.0	4.0	-1.0	1.0	1.0
4.0	2.0	2.0	1.0	-1.0	-1.0
4.0	2.0	4.0	1.0	-1.0	1.0
4.0	4.0	2.0	1.0	1.0	-1.0
4.0	4.0	4.0	1.0	1.0	1.0
1.5	3.0	3.0	-1.5	0.0	0.0
4.5	3.0	3.0	1.5	0.0	0.0
3.0	1.5	3.0	0.0	-1.5	0.0
3.0	4.5	3.0	0.0	1.5	0.0
3.0	3.0	1.5	0.0	0.0	-1.5
3.0	3.0	4.5	0.0	0.0	1.5
3.0	3.0	3.0	0.0	0.0	0.0

Note: Above $a_i' = a_i - 3.0$, $i=1,2,3$.

Table 6.9. R^2 Values and Final Fitted Component Amount Models for the "True" Surfaces (6.29) and (6.30)

Surface	R^2 Values for 1st Degree CA Model	R^2 Values for 2nd Degree CA Model	R^2 Values for Final* CA Model
(6.29)	0.918	0.995	0.989
(6.30)	0.804	0.991	0.987

Surface	Final* CA Models
(6.29)	$\hat{y} = 31.33 + 0.16a_1' + 4.12a_2' + 0.36a_3' - 1.31a_1'a_2' + 0.63(a_1')^2$
(6.30)	$\hat{y} = 30.80 - 0.57a_1' + 3.56a_2' - 0.31a_3' - 1.38a_1'a_2' + 0.85a_1'a_3' - 0.64a_2'a_3' + 1.29(a_1')^2$

* Final models always contain the terms α_0, $\alpha_1 a_1'$, $\alpha_2 a_2'$, and $\alpha_3 a_3'$ and any of the second-degree terms which are significant.

general it appears that the polynomial component amount models are of very little help in suggesting the presence of an additive blending component.

To summarize the results of this section, it appears that the polynomial component amount models approximate mixture-amount response surfaces very well, but offer little of the interpretative information that mixture-amount models provide. Hence, contrary to our earlier hypothesis that, for certain types of response behavior, mixture-amount models might provide a considerably better fit than polynomial component amount models, we conclude that the improvement (if any) over component amount models will usually be small. The gain in fitting the mixture-amount models lies in the interpretative information provided about the component blending properties and about the effect of the amount of the mixture on these properties.

CHAPTER SEVEN
EXAMPLES OF MIXTURE-AMOUNT, COMPONENT AMOUNT, AND COMPONENT-WISE MIXTURE EXPERIMENTS

In this chapter, we present an example of each of the three types of general mixture experiments discussed in the earlier chapters. In each example, the experimental design and the resulting data are given and an analysis using the corresponding model type is presented. In the mixture-amount and component amount examples, both types of models are fitted for reasons of comparison.

7.1 A Mixture-Amount Experiment Example

Claringbold (1955) presented the results of an experiment which involved the administration of mixtures of three hormones to groups of 12 mice. The hormone mixtures were administered in each of three amounts: 0.75, 1.50, and 3.00 (measured in units of 10^{-4} µg). The number of mice (out of 12) in each group that responded to a given mixture-amount combination were recorded and the percentage response, defined as a proportion p, was calculated. To these proportions, Claringbold applied the angular transformation

$$y = \begin{cases} \arcsin\sqrt{\frac{1}{4n}} = 8.30 & p = 0 \\ \arcsin\sqrt{p} & 0<p<1 \\ 90 - \arcsin\sqrt{\frac{1}{4n}} = 81.70 & p = 1 \end{cases}$$

where n = 12 above.

To simplify the discussion and analysis, we consider only the first of Claringbold's two "replicates" (blocks). The design [Scheffé (1958) later called this a {3,3} simplex-lattice design] that was set up at each of the three total amounts is pictured in Figure 7.1. The design points, proportions responding (p), and the angular transformed responses (y) are given in Table 7.1.

The mixture-amount design consisting of a {3,3} simplex-lattice at each of the three levels of total amount supports fitting (exactly) a mixture-amount model where η_C is a cubic Scheffé polynomial and $\beta_m(A)$ is a second-degree polynomial in A. However, in practice such a saturated model is usually not used (or necessary). The results of fitting several smaller mixture-amount models are given in Table 7.2. Note that the methods of computing the ANOVA tables and the statistics R^2 and R_A^2 as discussed by Marquardt and Snee (1974) are still valid, even though the form of the mixture model has been modified to include the effects of the total amount of the mixture.

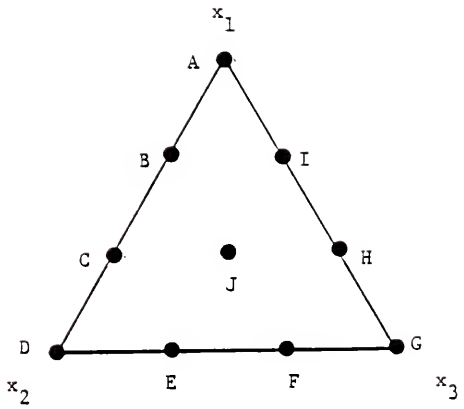


Figure 7.1. Claringbold's {3,3} Simplex-Lattice Design

Table 7.1. Design and Observations for Claringbold's Experiment

				% response (p)			angular response (y)		
				A =			A =		
Pt	x_1	x_2	x_3	.75	1.50	3.00	.75	1.50	3.00
A	1	0	0	.17	.42	.83	24.09	40.20	65.91
B	2/3	1/3	0	0	.33	.75	8.30	35.26	60.00
C	1/3	2/3	0	.33	.33	.75	35.26	35.26	60.00
D	0	1	0	.58	.58	1.00	49.80	49.80	81.70
E	0	2/3	1/3	.17	.33	.67	24.09	35.26	54.74
F	0	1/3	2/3	.33	.33	.58	35.26	35.26	49.80
G	0	0	1	.25	.50	.42	30.00	45.00	40.20
H	1/3	0	2/3	.25	.42	.42	30.00	40.20	40.20
I	2/3	0	1/3	0	.25	.75	8.30	30.00	60.00
J	1/3	1/3	1/3	.17	.25	.58	24.09	30.00	49.80

Table 7.2. Results of Fitting Several Mixture-Amount Models to Claringbold's Data

Model 1: $\sum_{k=0}^{2} \left[\sum_{i=1}^{3} \beta_i^k x_i + \sum_{i<j}^{3} \beta_{ij}^k x_i x_j \right] (A')^k$

SV	df	SS	
Total	29	7538.8	$R^2 = .917$
Model	17	6913.1	$R_A^2 = .800^*$
Error	12	625.7	

Model 2: $\sum_{k=0}^{1} \left[\sum_{i=1}^{3} \beta_i^k x_i + \sum_{i<j}^{3} \beta_{ij}^k x_i x_j \right] (A')^k$

SV	df	SS	
Total	29	7538.8	$R^2 = .889$
Model	11	6704.2	$R_A^2 = .822$
Error	18	834.6	

Model 3: $\sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{3} \beta_i^1 x_i A'$

SV	df	SS	
Total	29	7538.8	$R^2 = .886$
Model	8	6676.1	$R_A^2 = .842$
Error	21	862.7	

Model 4: $\sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \beta_{ij}^0 x_i x_j + \beta_0^1 A'$

SV	df	SS	
Total	29	7538.8	$R^2 = .785$
Model	6	5920.5	$R_A^2 = .729$
Error	23	1618.3	

Note: A' represents a coded form of the total amount variable A, given by $A' = (A - 1.75)$.

*R_A^2 = 1-(Error SS/Error df)/(Total SS/Total df)

Given the nature of the data, model 3 of Table 7.2 seems to provide a good fit with only 9 terms. The fitted model 3 is given by

$$\hat{y} = \underset{(3.48)}{41.90x_1} + \underset{(3.48)}{59.34x_2} + \underset{(3.48)}{40.34x_3} - \underset{(15.42)}{50.76x_1x_2} - \underset{(15.42)}{27.04x_1x_3}$$

$$- \underset{(15.42)}{47.02x_2x_3} + \underset{(2.80)}{21.40x_1A'} + \underset{(2.80)}{14.43x_2A'} + \underset{(2.80)}{2.99x_3A'} \qquad (7.1)$$

where $A' = A - 1.75$ and the quantities in parentheses below the coefficient estimates are their estimated standard errors. Under this coding, the levels of A (0.75, 1.5, 3.0) become -1.0, -0.25, and 1.25 (which have mean zero).

Recall from the discussion in Chapter 3 that, under the above coding, the mixture-only portion

$$41.90x_1 + 59.34x_2 + 40.34x_3 - 50.76x_1x_2$$

$$- 27.04x_1x_3 - 47.02x_2x_3 \qquad (7.2)$$

of (7.1) explains the linear and nonlinear blending properties of the three hormones at the average level of total amount. Since the model (7.1) only contains terms with a linear effect of A, the portion (7.2) may also be interpreted as the linear and nonlinear blending properties of the three hormones averaged over the three levels of amount. In particular, since a high percentage of mice responding is considered desirable, this portion of the

model alludes to the presence of antagonistic blending between hormones 1 and 2 as well as hormones 2 and 3 (the estimates of the coefficients of these crossproduct terms are significantly less than zero). That the coefficients of (7.2) represent the linear and nonlinear blending properties of the three hormones averaged over the three amounts can be verified by fitting a second-degree Scheffé polynomial separately for each of the three amounts,

$$\hat{y}_{A_1} = 17.95x_1 + 49.19x_2 + 34.66x_3 - 48.34x_1x_2 - 27.48x_1x_3 - 50.42x_2x_3$$

$$\hat{y}_{A_2} = 39.46x_1 + 49.15x_2 + 46.49x_3 - 40.95x_1x_2 - 35.69x_1x_3 - 56.76x_2x_3$$

$$\hat{y}_{A_3} = 68.28x_1 + 79.69x_2 + 39.88x_3 - 62.98x_1x_2 - 17.96x_1x_3 - 33.87x_2x_3 ,$$

and averaging the three coefficients for each term. Fitting a mixture model for each amount is a useful analysis technique in its own right, and can be used in developing an appropriate mixture-amount model. Graphical or WLS regression analysis of the estimated parameters of these separate models can suggest a form $\beta_m(A)$ for each parameter.

Since there are no terms involving $(A')^2$ in (7.1), we conclude that the effect of total amount on the blending of the three hormones is linear, not quadratic. The fact that we only have $x_i A'$ terms in (7.1) and not $x_i x_j A'$ terms says that the total amount affects only the linear blending properties of the three hormones and does not affect the nonlinear blending of the hormones. Noting that the $\hat{\beta}_i^1$'s ($\hat{\beta}_1^1 = 21.40$, $\hat{\beta}_2^1 = 14.43$, $\hat{\beta}_3^1 = 2.99$) are quite different in magnitude, we would surmise that changing the amount does indeed affect the component blending (in fact, the effect of increasing the amount is clearly more pronounced with hormone 1 than with hormone 3). The significance of including the three $\beta_i^1 x_i A'$ terms in the model is verified by considering model 4 in Table 7.2 to be a reduced form of model 3 and calculating the full vs. reduced model F* statistic given by (3.8),

$$F^* = \frac{(1618.3 - 862.7)/(23-21)}{862.7/21} = 9.20 ,$$

which is highly significant.

We now consider fitting polynomial component amount models to Claringbold's data. A summary of results from fitting several component amount models is given in Table 7.3. Models 2 and 4 in Table 7.3 are reduced forms of models 1 and 3 obtained by stepwise regression. We see that none of these models (not even the ones with third-degree terms) had R_A^2 values as large as the R_A^2 value for the

Table 7.3. Results of Fitting Component Amount Models to Claringbold's Data

Model 1: $\alpha_0 + \sum_{i=1}^{3} \alpha_i a_i + \sum_{i<j}^{3} \sum \alpha_{ij} a_i a_j + \sum_{i=1}^{3} \alpha_{ii} a_i^2$

SV	df	SS	
Total	29	7538.8	$R^2 = .825$
Model	9	6217.6	$R_A^2 = .746$
Error	20	1321.2	

Model 2: $\alpha_0 + \sum_{i=1}^{3} \alpha_i a_i + \alpha_{23} a_2 a_3 + \alpha_{11} a_1^2 + \alpha_{33} a_3^2$ (a)

SV	df	SS	
Total	29	7538.8	$R^2 = .823$
Model	6	6200.9	$R_A^2 = .776$
Error	23	1337.9	

(a) Obtained by stepwise regression allowing at most second degree terms.

Model 3: Cubic polynomial in the a_i (b)

SV	df	SS	
Total	29	7538.8	$R^2 = .917$
Model	18	6915.6	$R_A^2 = .782$
Error	11	623.2	

(b) Extreme collinearity forced deleting the term with $a_3^2 a_2$.

Model 4: $\alpha_0 + \sum_{i=1}^{3} \alpha_i a_i + \alpha_{23} a_2 a_3 + \alpha_{11} a_1^2 + \alpha_{111} a_1^3 + \alpha_{333} a_3^3$ (c)

SV	df	SS	
Total	29	7538.8	$R^2 = .856$
Model	7	6449.8	$R_A^2 = .810$
Error	22	1089.0	

(c) Obtained by stepwise regression allowing at most third degree terms.

mixture-amount model (7.1). It should be noted, however, that Claringbold's design (a mixture-amount design) is far from optimal for the polynomial component amount models. This is a limitation in fitting component amount models and in comparing the two modeling approaches for this data.

In closing this section, it should be mentioned that Claringbold did not fit either of the two types of models (mixture-amount or component amount) we have considered. Instead, he transformed the mathematically dependent variables x_1, x_2, x_3 to mathematically independent variables which we denote by W_1 and W_2. Using our notation (A') for the coded total amount variable, his model (for the first "replicate") has the form

$$\eta = \gamma_0^0 + \gamma_1^0 W_1 + \gamma_2^0 W_2 + \gamma_{12}^0 W_1 W_2 + \gamma_{11}^0 W_1^2 + \gamma_{22}^0 W_2^2 + \gamma_0^1 A' + \gamma_1^1 W_1 A' + \gamma_2^1 W_2 A' \,. \tag{7.3}$$

This model provides a fit equivalent to that of (7.1) when the coding $A' = A - 1.75$ is used. Claringbold coded the levels of A (0.75, 1.5, and 3.0) as -1, 0, +1, implying a belief that the effects of A are logarithmic. A mixture-amount model similar to (7.1), except with A' replaced by $(\log A)'$, did not fit as well as did (7.1).

Finally, although we do not discuss it here, we note that the experiment of Bliss (1939) is another example of a mixture-amount experiment.

7.2 A Component Amount Experiment Example

Suich and Derringer (1977) presented the results of a two-component rubber abrasion resistance study. The purpose of the study was to relate silica filler level, a_1, and coupling agent level, a_2, to abrasion resistance of rubber, y. A central composite design plus additional corner and center points were used. The levels of a_1 and a_2 along with the levels of the coded variables a_1' and a_2', and the data values are listed in Table 7.4. Suich and Derringer fitted a second-degree polynomial (component amount model) in the coded variables a_1' and a_2', obtaining

$$\hat{y} = \underset{(1.44)}{97.72} + \underset{(0.78)}{5.87}a_1' + \underset{(0.78)}{6.04}a_2' + \underset{(0.60)}{2.83}a_1'a_2' - \underset{(1.01)}{0.11}(a_1')^2 - \underset{(1.01)}{3.89}(a_2')^2 \quad . \tag{7.4}$$

The corresponding ANOVA table is given in Table 7.5. Suich and Derringer noted that the lack of fit was not significant at the $\alpha = .05$ level. However, it is significant at the $\alpha = .10$ level, and so we considered fitting third-degree polynomial component amount models. Stepwise regression yielded the fitted equation

Table 7.4. Abrasion Resistance of Rubber Data from Suich and Derringer (1977)

a_1	a_2	a_1'	a_2'	y
56.67	2	1	-1	83
56.67	6	1	1	113
43.33	6	-1	1	92
43.33	2	-1	-1	82
50	4	0	0	100
50	4	0	0	96
50	4	0	0	98
50	7	0	1.5	95
50	1	0	-1.5	80
60	4	1.5	0	100
40	4	-1.5	0	92
60	1	1.5	-1.5	87
60	7	1.5	1.5	110
40	1	-1.5	-1.5	79
40	7	-1.5	1.5	84
40	7	-1.5	1.5	79
40	1	-1.5	-1.5	75
60	7	1.5	1.5	117
60	1	1.5	-1.5	84
50	4	0	0	100
50	4	0	0	102
50	4	0	0	96

Note: Above $a_1' = \frac{a_1 - 50}{20/3}$ and $a_2' = \frac{a_2 - 4}{2}$.

Table 7.5. ANOVA Table for the Fitted Second-Degree Polynomial Component Amount Model (7.4)

Source	df	SS	MS	F
Total	21	2845.82	--	
Regression	5	2587.55	517.51	
Residual	16	258.26	16.14	
Lack of Fit	7	179.43	25.63	2.93*
Pure Error	9	78.83	8.76	

* The lack of fit is significant at the p = .068 level.

Table 7.6. ANOVA Table for the Fitted Third-Degree Polynomial Component Amount Model (7.5)

Source	df	SS	MS	F
Total	21	2845.82	--	
Regression	6	2718.85	453.14	
Residual	15	126.97	8.46	
Lack of Fit	6	48.14	8.02	0.92
Pure Error	9	78.83	8.76	

$$\hat{y} = \underset{(0.96)}{97.66} + \underset{(1.22)}{3.05a_1'} + \underset{(2.66)}{13.73a_2'} + \underset{(0.44)}{2.83a_1'a_2'}$$

$$- \underset{(0.61)}{3.95(a_2')^2} + \underset{(0.64)}{1.68(a_1')(a_2')^2} - \underset{(1.26)}{3.73(a_2')^3} . \qquad (7.5)$$

The corresponding ANOVA table is given in Table 7.6, where it is seen that (7.5) has a nonsignificant lack of fit at the $\alpha = .10$ level.

We now consider the fitting of canonical polynomial mixture-amount models to see if an informative interpretation about component blending and how the total amount affects component blending can be obtained. The variables in the fitted model are defined by applying a L-pseudo-component transformation

$$x_1' = \frac{x_1 - .8511}{.1325} \qquad x_2' = \frac{x_2 - .0164}{.1325} \qquad (7.6)$$

to the component proportions and a standardizing transformation

$$A' = \frac{A - 54}{13} \qquad (7.7)$$

to the total amount. Several canonical polynomial mixture-amount models were fitted; the following model provided the best fit while having all coefficients significant:

$$\hat{y} = \underset{(1.44)}{81.33}x_1' + \underset{(7.42)}{58.33}x_2' + \underset{(16.69)}{124.62}x_1'x_2' - \underset{(26.36)}{115.34}x_1'x_2'(x_1'-x_2')$$
$$+ \underset{(2.42)}{7.32}x_1'A' - \underset{(13.91)}{42.65}x_2'A' + \underset{(32.00)}{124.09}x_1'x_2'A'$$
$$- \underset{(36.40)}{138.31}x_1'x_2'(x_1'-x_2')A' . \qquad (7.8)$$

The ANOVA table corresponding to this fitted mixture-amount model is given in Table 7.7. The fitted model (7.8) indicates that the component blending is nonlinear (cubic) at the average level of total amount. Moreover, the total amount has a linear effect on the linear and nonlinear component blending properties.

As for the specific types of component blending at the different levels of total amount, note in (7.8) that $\hat{\beta}^0_{12}(= 124.62) \approx \hat{\beta}^1_{12}(= 124.09)$ and $\hat{\delta}^0_{12}(= -115.34) \approx \hat{\delta}^1_{12}(= -138.31)$. This suggests (see Appendix B) the possibility that the component blending is linear for $A' = -1$ ($A = 41$), and becomes increasingly nonlinear as A' approaches $+1$ ($A = 67$). We reserve judgement about strongly inferring the presence of linear blending at $A' = -1$, however, since there is only one point in the component amount design with $A' = -1$, and this point is at an extreme corner of the rectangular constraint region. However, if we choose to follow up on our observation, we can fit a reduced form of (7.8), where now we assume

Table 7.7. ANOVA Table for the Fitted Cubic by Linear Mixture-Amount Model (7.8)

Source	df	SS	MS	F
Total	21	2845.82	--	
Regression	7	2754.91	393.56	
Residual	14	90.91	6.49	
Lack of Fit	5	12.08	2.42	0.28
Pure Error	9	78.83	8.76	

Table 7.8. ANOVA Table for the Fitted Cubic by Linear Mixture-Amount Model Under the Restrictions (7.9)

Source	df	SS	MS	F
Total	21	2845.82	--	
Regression	5	2751.44	550.29	
Residual	16	94.38	5.90	
Lack of Fit	7	15.55	2.22	0.25
Pure Error	9	78.83	8.76	

$$\beta_{12}^{0} = \beta_{12}^{1} \quad \text{and} \quad \delta_{12}^{0} = \delta_{12}^{1} \; . \tag{7.9}$$

The fitted model under this assumption is given by

$$\begin{aligned}\hat{y} = {} & \underset{(1.13)}{81.76x_1'} + \underset{(4.72)}{59.32x_2'} + \underset{(1.60)}{6.25x_1'A'} - \underset{(7.46)}{40.15x_2'A'} \\ & + \underset{(12.20)}{121.79x_1'x_2'(1+A')} - \underset{(18.05)}{118.40x_1'x_2'(x_1'-x_2')(1+A')} \; . \end{aligned} \tag{7.10}$$

The associated ANOVA table is given in Table 7.8. The full versus reduced model F-statistic is

$$F^* = \frac{(94.38 - 90.91)/(16 - 14)}{94.38/16} = 0.29 \; ,$$

which supports the assumption (7.9).

In comparing the fitted component amount and mixture-amount models (7.5) and (7.10), respectively, it is interesting to note that the mixture-amount model (7.10) explained more of the variability in the data [R^2 = .967 for (7.10) versus R^2 = .955 for (7.5)] and used fewer terms in doing so (6 versus 7) than did the component amount model (7.5). This is especially surprising in view of the fact that the data were collected on a rectangular component amount design/constraint region, and previously in Section 6.3 we had observed with an example that multicollinearity problems can arise when fitting mixture-amount models to data collected from a region like this. In spite of this,

the mixture-amount model (7.10) seems to provide a slightly better fit than the component amount model (7.5). In addition, the mixture-amount model gives the nice interpretation that component blending is essentially linear at $A' = -1$, and becomes nonlinear (cubic) as A' increases to +1.

7.3 A Component-Wise Mixture Experiment Example

Unfortunately, a component-wise mixture example could not be found in the literature. To serve as an example, a portion of the data from the rubber abrasion resistance study of Suich and Derringer (1977) considered in the previous section is used. Suppose in that study that the component amounts cannot range freely between their bounds

$$40 \leq a_1 \leq 60 \quad \text{and} \quad 1 \leq a_2 \leq 7 \ , \tag{7.11}$$

and that only fractional combinations of the base values $a_1^0 = 190/3$ and $a_2^0 = 19$ which satisfy (7.11) are of interest. Mathematically, this restriction is written as

$$\frac{1}{190/3} a_1 + \frac{1}{19} a_2 = 1 \ , \tag{7.12}$$

as per equation (5.9) in Chapter 5. The twelve points (five distinct) from the Suich and Derringer data that satisfy (7.11) and (7.12) are listed in Table 7.9.

Table 7.9. Data for the Component-Wise Mixture Experiment Example

a_1	a_2	x_1^*	x_2^*	$(x_1^*)'$	$(x_2^*)'$	y
60	1	.9474	.0526	1.0000	.0000	87
60	1	.9474	.0526	1.0000	.0000	84
56.67	2	.8947	.1053	.8333	.1667	83
50	4	.7895	.2105	.5000	.5000	100
50	4	.7895	.2105	.5000	.5000	96
50	4	.7895	.2105	.5000	.5000	98
50	4	.7895	.2105	.5000	.5000	100
50	4	.7895	.2105	.5000	.5000	102
50	4	.7895	.2105	.5000	.5000	96
43.33	6	.6842	.3158	.1667	.8333	92
40	7	.6316	.3684	.0000	1.0000	84
40	7	.6316	.3684	.0000	1.0000	79

Note: The primes above indicate L-pseudocomponent transformations, defined by

$$(x_1^*)' = \frac{x_1^* - .6316}{.3158}$$

and

$$(x_2^*)' = \frac{x_2^* - .0526}{.3158} \quad .$$

We consider models in the component-wise proportions transformed using the L-pseudocomponent transformation (see Table 7.9). The cubic canonical polynomial model

$$\hat{y} = \underset{(2.18)}{84.68(x_1^*)'} + \underset{(2.18)}{80.68(x_2^*)'} + \underset{(8.10)}{61.21(x_1^*)'(x_2^*)'} - \underset{(26.52)}{63.00(x_1^*)'(x_2^*)'[(x_1^*)'-(x_2^*)']} \qquad (7.13)$$

has a nonsignificant lack of fit at the $\alpha = .05$ level. The ANOVA table corresponding to the fitted model (7.13) is given in Table 7.10. The fact that the lack of fit becomes significant at $p = .062$ suggests that a quartic (saturated) model might be considered. That such a high degree model may be necessary is somewhat bothersome, and suggests that the two unreplicated points be checked (in particular the point at $a_1 = 56.6667$ and $a_2 = 2$, with response 83).

Although it is usually not possible to compare a fitted component-wise mixture model to a fitted mixture-amount or component amount model, it is possible here because the component-wise experiment data in Table 7.9 are from a larger (dimension-wise) component amount design. Fitted mixture-amount and component amount models for the larger design (given in Table 7.4) were presented in equations (7.10) and (7.5), respectively. These fitted models can be used to make predictions for the twelve component-wise mixture design points (given in Table 7.9), and these

Table 7.10. ANOVA Table for the Fitted Component-Wise Mixture Model (7.13)

Source	df	SS	MS	F
Total	11	698.25	--	
Regression	3	619.31	206.44	
Residual	8	78.94	9.87	
Lack of Fit	1	32.61	32.61	4.92*
Pure Error	7	46.33	6.62	

* The lack of fit is significant at the p = .062 level.

predictions can be compared to the observed abrasion resistance values to see which type of model does the best job of predicting at these twelve points. As a metric to compare predicted to observed values, we use the prediction error sum of squares $\sum_{i=1}^{12}(y_i-\hat{y}_i)^2$. Values of this statistic equal to 78.94, 59.43, and 81.42 are obtained using the fitted models (7.13), (7.10), and (7.5), respectively. The value 59.43, which corresponds to the mixture-amount model (7.10), is considerably lower than the values for the other models (keeping in mind that the lower bound for these values is the pure-error sum of squares 46.33 from Table 7.10). This result seems to suggest that, if possible, one should consider performing a mixture-amount experiment instead of a component-wise mixture experiment. Of course, this is not always possible in practice.

CHAPTER EIGHT
SUMMARY AND RECOMMENDATIONS

Study and research in the area of mixture experiments has been going on for almost 30 years now. During this time, it has been assumed (by the definition of a mixture experiment) that the response to a mixture is affected only by the proportions of the components in the mixture, and not by the total amount of the mixture. In practice, this assumption is often obviated by fixing the total amount of the mixture.

In contrast, there are many applications where the total amount of the mixture does affect the response. There are other applications where it is unknown whether or not the total amount affects the response. The purpose of this work is to extend the definition/concept of a mixture experiment to encompass these kinds of applications, and to present and compare designs and models for investigating these kinds of applications.

In the first section below, the major findings of this work are summarized. Based on these findings, recommendations are made in the second section as to when various experimental approaches should be used.

8.1 Summary

A general mixture experiment was defined in Section 1.3 as an experiment in which two or more components are mixed, and where the response is assumed to be a function of the component proportions and possibly the total amount of the mixture. A mixture experiment, as defined by Scheffé (1958), is obviously a special case of the general mixture experiment, where the amount of the mixture is held constant or where the response does not depend on the level of the total amount. Three other types of experiments, referred to as mixture-amount, component amount, and component-wise mixture experiments, were also seen to be general mixture experiments.

Mixture-amount experiments were discussed in Chapters 3 and 4. A mixture-amount experiment consists of a series of mixture experiments conducted at each of two or more levels of total amount. Mixture-amount models were developed in Chapter 3 by considering the parameters of mixture models as functions of the total amount of the mixture. This class of models is quite broad, in that any mixture model (see Section 2.1) can be used as a starting point, and the parameters can be expressed as any function of the total amount. Examples of canonical polynomial mixture-amount models are presented in Appendices A and B.

Designs for both unconstrained and constrained mixture-amount experiments were discussed in Chapter 4. The

mixture-amount designs suggested were mixture designs set up at each level of total amount, where the mixture designs at the different levels of total amount may or may not be the same. Methods of fractionating mixture-amount designs were discussed in Section 4.2. A computer-aided design approach was seen to be the most flexible fractionation method. The DETMAX computer-aided design program of Mitchell (1974), based on the D_N-optimality criterion, was used to perform design fractionation for this work. Using DETMAX, three component D_N-optimal designs for various canonical polynomial mixture-amount models were constructed and are presented in Appendix C. Based on the resulting designs, sequential D_N-optimal design development procedures were formulated and presented in Tables 4.4 - 4.12.

Component amount experiments (the second kind of general mixture experiment) were discussed in Section 5.1. In this type of experiment, standard response surface designs (e.g., factorial, fractional factorial, and central composite) in the component amounts are used, with standard polynomial forms in the component amounts used to model the surface.

Component-wise mixture experiments (the third kind of general mixture experiment) were discussed in Section 5.2. Designs and models for this type of experiment are similar to those used for mixture experiments, except that the proportions are computed on a component-wise basis instead

of a total amount basis as with the usual mixture experiments. Component-wise mixture experimental designs and models may also be formulated in terms of the component amount variables, where the combinations of amounts of the components are limited by a restriction on the response or some other property of interest. The restriction is defined in terms of base values of each component, which are the amounts of the pure components that yield the desired response or property value.

Mixture-amount, component amount, and component-wise mixture experiments were compared in Chapter 6 on the basis of the constraint regions, designs, and models felt to be appropriate for each type of experiment. It was noted that the constraint region of a component-wise mixture experiment is of dimensionality one less than the constraint regions of mixture-amount and component amount experiments with the same number of components, and hence a component-wise mixture experiment is not directly comparable to the other two types of experiments.

A component-wise mixture experiment is directly comparable to a mixture experiment, since the constraint regions of these two types of experiments are of the same dimensionality. The difference between a component-wise mixture experiment and a normal mixture experiment is that the total amount of the mixture varies and is assumed to affect the response in the former; while in the latter, the

total amount is held fixed or is assumed not to affect the response. While component-wise mixture experiments allow for the total amount affecting the response, component-wise mixture designs and models do not provide ways for testing (independently of the effects of the component proportions) whether or not the total amount does indeed affect the response.

Mixture-amount and component amount experiments have constraint regions of the same dimensionality (for a fixed number of components) and hence are directly comparable. Constraint regions for these two types of general mixture experiments were compared in Section 6.1, where it was seen that they have different configurations and orientations (and hence cover different subregions of the space of all mixture-amount combinations).

Mixture-amount and component amount models were compared in Section 6.2. Mixture-amount models (under appropriate codings) contain terms which represent the linear and nonlinear blending properties of the components at the average level of total amount (or averaged over all levels of total amount), while other terms describe how varying the amount of the mixture affects the component blending properties. In this sense, the mixture-amount models separate the component blending information and the amount effect information. The polynomial component amount models do not separate these two types of information, since they

are based on the $a_i = x_iA$, $i=1,2, \ldots ,q$ (where A is the uncoded total amount variable).

Mixture-amount and component amount models were further compared in Section 6.2 by rewriting mixture-amount models in terms of the component amounts a_i. Canonical mixture-amount models were seen to be expanded forms of polynomial component amount models, where the extra terms in the rewritten mixture-amount models are nonpolynomial functions of the component amount variables. In general, rewriting any mixture-amount model in terms of the component amount variables yields a nonpolynomial function of the a_i's. This raised the question as to whether mixture-amount model forms might describe some response surfaces better than polynomial component amount model forms. The ability of polynomial component amount model forms to satisfactorily approximate several hypothetical "true" mixture-amount surfaces was investigated in Section 6.4. Overall, the polynomial model forms did a good job of approximating mixture-amount surfaces.

Mixture-amount and component amount designs were compared in Section 6.3. In general, each type of design is preferred for generating data values with which to fit its own particular type of model. However, our interest was in seeing how much support one type of design provides for the other type of model. In particular, we were interested in knowing if it is possible to learn something about the

component blending properties and how varying the total amount affects these properties, even when the data are from a component amount design. As expected (because of the different configurations and orientations of the constraint regions), multicollinearity problems arise when trying to fit a mixture-amount model to a component amount design. Multicollinearity problems also occur (but to a somewhat lesser extent) when trying to fit a component amount model to a mixture-amount design. If the multicollinearity problems are severe, the attendant variance inflation of the parameter estimates can render some or all of the parameter estimates meaningless. For situations where the multicollinearity problems are not too bad, some information about the component blending properties and how the total amount effects these blending properties can be obtained by fitting mixture-amount models to a component amount design. This information should be considered with caution, and care should be taken not to attach too much meaning to the estimated parameters.

An example of each of the three types of general mixture experiments (mixture-amount, component amount, and component-wise mixture) was presented in Chapter 7. For the component amount experiment example, a mixture-amount model provided a nice interpretation and explained slightly more of the variability in the data than did the component amount model.

8.2 Recommendations

Based on the findings of this work, which were summarized in the previous section, recommendations are made as to when each of the three kinds of general mixture experiments (mixture-amount, component amount, and component-wise mixture) should be utilized. Recommendations are also made as to which kinds of models should be fitted when data from a specific kind of design is available.

The differences in configuration and orientation of mixture-amount and component amount constraint regions (discussed in Section 6.1) relates to the differences in interpretative understanding the two approaches provide. The mixture-amount approach attempts to explain the behavior of the response in terms of the component proportions and the total amount of the mixture, while the component amount approach attempts to explain the response behavior in terms of the component amounts. On the other hand, the comparison of mixture-amount and component amount models in Sections 6.2 and 6.4 turned up no major differences in terms of the ability of the two types of models to approximate various response surfaces. Hence, it is the differences in interpretative understanding of the two approaches that should be the basis of our recommendations.

A mixture-amount experimental approach is recommended if the experimenter is interested in understanding how the components blend and how varying the amount of the mixture

affects the component blending. If the experimenter is not interested in this sort of information but only wants to know how much of each component should be mixed to obtain the optimum response, then the component amount experimental approach would suffice. [As a note in passing, the mixture-amount approach can also provide information about the optimum amounts of the components.] The fact that the mixture-amount experimental approach allows for a fuller understanding of the underlying response surface than does the component amount approach, suggests it is the preferable approach in this author's opinion.

A component-wise mixture experimental approach will be required if there is some restriction on the response (or some other property of interest) that imposes a linear constraint on the amounts of the components. However, if there is sufficient flexibility in the restriction to allow mixtures to be run at more than one total amount, then a mixture-amount experimental approach is recommended. More experimental effort may be required with the mixture-amount approach, since its constraint region will be of dimensionality one higher than that for the component-wise mixture approach. However, this extra effort allows for testing and understanding the effect of the total amount on the response (which the component-wise mixture approach does not).

We now turn attention to recommendations of which model forms should be fitted when data from a certain type of

design (mixture-amount, component amount, or component-wise mixture) is available. Of course, it is always recommended that models of the same type as the design be fitted. However, it may also be of value to fit models of other types.

For data from a component amount design, it is recommended that mixture-amount models also be fitted (with levels of A, log A, etc. coded to have mean zero) because of the interpretative information such models provide. Variance inflation factors should be computed for the mixture-amount models considered, to see how severe the multicollinearity problems are. If the multicollinearity is not too bad, the mixture-amount models can provide some information about how the components blend and how the amount of the mixture affects the component blending.

The reasons for fitting component amount models to data from a mixture-amount design are not so clear. For some situations, a component amount model might provide a similar or slightly better fit than a mixture-amount model, but with fewer terms. Although such situations are not expected to occur too often, when they do occur the component amount model may be preferred for predictive purposes, with the mixture-amount model still providing an understanding of component blending and the effect of total amount.

For data from a component-wise mixture design, it is not possible to fit mixture-amount or component amount

models. However, it is possible (and recommended) that the usual mixture model forms in the component proportions be fitted to the data. If the total amount of the mixture does not affect the response, then the usual mixture model forms are appropriate.

APPENDIX A
SCHEFFÉ CANONICAL POLYNOMIAL MIXTURE-AMOUNT MODELS

Various Scheffé canonical polynomial mixture-amount models are listed and discussed in this appendix. The models presented are thought to be those of most interest in practice.

A.1 Models in Which the Components Blend Linearly

Consider the following Scheffé canonical polynomial mixture-amount models where the components blend linearly.

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \beta_0^1 A' \tag{A.1}$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_i^1 x_i A' \tag{A.2}$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \beta_0^1 A' + \beta_0^2 (A')^2 \tag{A.3}$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_i^1 x_i A' + \beta_0^2 (A')^2 \tag{A.4}$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i=1}^{q} \beta_i^2 x_i (A')^2 \tag{A.5}$$

Situations in which these models are appropriate are given below.

(A.1): The total amount does not affect component blending, but does have a linear effect on the response.

(A.2): The total amount has a linear effect on the linear blending properties of the components.

(A.3): The total amount does not affect component blending, but does have a quadratic effect on the response.

(A.4): The total amount has a linear effect on the linear blending properties of the components along with a quadratic effect on the response.

(A.5): The total amount has a quadratic effect on the linear blending properties of the components.

Note in (A.3) and (A.5), that although the effect of total amount is referred to as quadratic, the corresponding linear terms are also present in the model.

A.2 Models in Which the Components Blend Nonlinearly

Consider the following mixture-amount models based on the second-degree Scheffé canonical polynomial (2.4).

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \beta_0^1 A' \qquad \text{(A.6)}$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' \qquad \text{(A.7)}$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \sum \beta_{ij}^1 x_i x_j A' \qquad (A.8)$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \beta_0^1 A' + \beta_0^2 (A')^2 \qquad (A.9)$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \beta_0^2 (A')^2 \qquad (A.10)$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \sum \beta_{ij}^1 x_i x_j A' + \beta_0^2 (A')^2 \qquad (A.11)$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i=1}^{q} \beta_i^2 x_i (A')^2 \qquad (A.12)$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \sum \beta_{ij}^1 x_i x_j A' + \sum_{i=1}^{q} \beta_i^2 x_i (A')^2 \qquad (A.13)$$

$$\eta = \sum_{i=1}^{q} \beta_i^0 x_i + \sum_{i<j}^{q} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{q} \beta_i^1 x_i A' + \sum_{i<j}^{q} \beta_{ij}^1 x_i x_j A'$$

$$+ \sum_{i=1}^{q} \beta_i^2 x_i (A')^2 + \sum_{i<j}^{q} \beta_{ij}^2 x_i x_j (A')^2 \qquad \text{(A.14)}$$

Situations in which these models are appropriate are given below.

(A.6): The total amount does not affect component blending, but does have a linear effect on the response.

(A.7): The total amount has a linear effect on the linear blending properties of the components.

(A.8): The total amount has a linear effect on the linear and nonlinear blending properties of the components.

(A.9): The total amount does not affect component blending, but does have a quadratic effect on the response.

(A.10): The total amount has a linear effect on the linear blending properties of the components. In addition, the total amount has a quadratic effect on the response.

(A.11): The total amount has a linear effect on the linear and nonlinear blending properties of the components. In addition, the total amount has a quadratic effect on the response.

(A.12): The total amount has a quadratic effect on the linear blending properties of the components.

(A.13): The total amount has a linear effect on the linear and nonlinear blending properties of the components. In addition, the total amount has a quadratic effect on the linear blending properties of the components.

(A.14): The total amount has a quadratic effect on the linear and nonlinear blending properties of the components.

Note in (A.9), (A.12), and (A.14), that although the effect of total amount is referred to as quadratic, the corresponding linear terms are also present in the model.

For certain applications, it may prove useful to consider models (similar to those above) based on the Scheffé full or special cubic canonical polynomial models (see Section 2.1). We shall not present these model forms here, since they are simple extensions of the forms (A.1) - (A.14).

APPENDIX B
MIXTURE-AMOUNT MODELS WHEN THE CANONICAL POLYNOMIAL FORM IS NOT THE SAME AT ALL LEVELS OF TOTAL AMOUNT

For simplicity, in this appendix we consider mixture-amount model forms for the cases of two and three components, where A takes on two or three levels. The results for q = 2 and 3 components readily extend to larger numbers of components.

B.1 Linear and Quadratic Blending at Two Amounts

It will be helpful to consider the most general situation for two amounts:

$$\eta_{A'=-1} = ax_1 + bx_2 + cx_1x_2$$

$$\eta_{A'=+1} = dx_1 + ex_2 + fx_1x_2 \quad , \tag{B.1}$$

where the two levels of A are coded as -1 and +1. The notation A' is used to denote the coded version of the total amount variable A. The mixture-amount model appropriate for this situation is

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_{12}^0 x_1x_2$$

$$+ \beta_1^1 x_1A' + \beta_2^1 x_2A' + \beta_{12}^1 x_1x_2A' \quad . \tag{B.2}$$

Substituting the data

x_1	x_2	A'	η
1	0	-1	a
0	1	-1	b
.5	.5	-1	(2a+2b+c)/4
1	0	1	d
0	1	1	e
.5	.5	1	(2d+2e+f)/4

into (B.2), the following system of equations is obtained.

$$\beta_1^0 - \beta_1^1 = a$$

$$\beta_2^0 - \beta_2^1 = b$$

$$\tfrac{1}{2}\beta_1^0 + \tfrac{1}{2}\beta_2^0 + \tfrac{1}{4}\beta_{12}^0 - \tfrac{1}{2}\beta_1^1 - \tfrac{1}{2}\beta_2^1 - \tfrac{1}{4}\beta_{12}^1 = (2a+2b+c)/4$$

$$\beta_1^0 + \beta_1^1 = d$$

$$\beta_2^0 + \beta_2^1 = e$$

$$\tfrac{1}{2}\beta_1^0 + \tfrac{1}{2}\beta_2^0 + \tfrac{1}{4}\beta_{12}^0 + \tfrac{1}{2}\beta_1^1 + \tfrac{1}{2}\beta_2^1 + \tfrac{1}{4}\beta_{12}^1 = (2d+2e+f)/4$$

Solving these equations simultaneously yields the solutions

$$\beta_1^0 = \frac{d+a}{2} \qquad \beta_2^0 = \frac{e+b}{2} \qquad \beta_{12}^0 = \frac{f+c}{2}$$

$$\beta_1^1 = \frac{d-a}{2} \qquad \beta_2^1 = \frac{e-b}{2} \qquad \beta_{12}^1 = \frac{f-c}{2} \quad . \qquad \text{(B.3)}$$

Note that the β_1^0, β_2^0, and β_{12}^0 coefficients measure the linear and nonlinear component blending properties averaged over the two levels of total amount. Equivalently, these coefficients may be interpreted as measuring the blending properties at the average level of total amount.

Now, consider the special case of the situation given by (B.1) where the components blend nonlinearly (quadratically) at the high level of A and linearly at the low level of A [i.e., c = 0 in (B.1)]. Substituting c = 0 in the solutions (B.3) yields the revised estimates β_{12}^0 = f/2 and β_{12}^1 = f/2. Hence, the appropriate mixture-amount model for this situation is of the form (B.2), where β_{12}^1 = β_{12}^0, i.e.,

$$\eta = \beta_1^0 x_1 + \beta_2^0 x_2 + \beta_1^1 x_1 A' + \beta_2^1 x_2 A' + \beta_{12}^1 x_1 x_2 (1+A') \quad . \tag{B.4}$$

The restriction becomes $\beta_{12}^1 = -\beta_{12}^0$ if the linear blending occurs at the high level of A and the nonlinear (quadratic) blending occurs at the low level of A.

B.2 Linear, Quadratic, and Quadratic Blending at Three Amounts

It will be helpful to consider the most general situation for three amounts,

$$\eta_{A'=-1} = ax_1 + bx_2 + cx_1x_2$$

$$\eta_{A'=0} = dx_1 + ex_2 + fx_1x_2$$

$$\eta_{A'=+1} = gx_1 + hx_2 + kx_1x_2 \quad , \tag{B.5}$$

where the three levels of A are coded as -1, 0, and +1. The notation A' is used to denote the coded version of the total amount variable A. The mixture-amount model appropriate for this general situation is

$$\eta = \sum_{k=0}^{2} [\beta_1^k x_1 + \beta_2^k x_2 + \beta_{12}^k x_1 x_2](A')^k \quad . \tag{B.6}$$

Substituting the data

x_1	x_2	A'	η
1	0	-1	a
0	1	-1	b
.5	.5	-1	(2a+2b+c)/4
1	0	0	d
0	1	0	e
.5	.5	0	(2d+2e+f)/4
1	0	1	g
0	1	1	h
.5	.5	1	(2g+2h+k)/4

into (B.6), the following system of equations is obtained.

$$\beta_1^0 - \beta_1^1 + \beta_1^2 = a$$

$$\beta_2^0 - \beta_2^1 + \beta_2^2 = b$$

$$\tfrac{1}{2}\beta_1^0 + \tfrac{1}{2}\beta_2^0 + \tfrac{1}{4}\beta_{12}^0 - \tfrac{1}{2}\beta_1^1 - \tfrac{1}{2}\beta_2^1 - \tfrac{1}{4}\beta_{12}^1 + \tfrac{1}{2}\beta_1^2 + \tfrac{1}{2}\beta_2^2 + \tfrac{1}{4}\beta_{12}^2 = (2a+2b+c)/4$$

$$\beta_1^0 = d$$

$$\beta_2^0 = e$$

$$\tfrac{1}{2}\beta_1^0 + \tfrac{1}{2}\beta_2^0 + \tfrac{1}{4}\beta_{12}^0 = (2d+2e+f)/4$$

$$\beta_1^0 + \beta_1^1 + \beta_1^2 = g$$

$$\beta_2^0 + \beta_2^1 + \beta_2^2 = h$$

$$\tfrac{1}{2}\beta_1^0 + \tfrac{1}{2}\beta_2^0 + \tfrac{1}{4}\beta_{12}^0 + \tfrac{1}{2}\beta_1^1 + \tfrac{1}{2}\beta_2^1 + \tfrac{1}{4}\beta_{12}^1 + \tfrac{1}{2}\beta_1^2 + \tfrac{1}{2}\beta_2^2 + \tfrac{1}{4}\beta_{12}^2 = (2g+2h+k)/4$$

Solving these equations yields the solutions

$$\beta_1^0 = d \qquad \beta_2^0 = e \qquad \beta_{12}^0 = f$$

$$\beta_1^1 = \frac{g-a}{2} \qquad \beta_2^1 = \frac{h-b}{2} \qquad \beta_{12}^1 = \frac{k-c}{2}$$

$$\beta_1^2 = \frac{g+a-2d}{2} \qquad \beta_2^2 = \frac{h+b-2e}{2} \qquad \beta_{12}^2 = \frac{k+c-2f}{2} . \quad (B.7)$$

Note that the β_1^0, β_2^0, and β_{12}^0 coefficients measure the linear and nonlinear component blending properties at the average (middle) level of total amount (owing to the coding of the three levels of A as -1, 0, and +1). Although we

make no use of them in this appendix, it is interesting to consider the solutions that are obtained when A' and $(A')^2$ in (B.6) are replaced by the first and second-degree orthogonal polynomials:

$$\beta_1^0 = \frac{a+d+g}{3} \qquad \beta_2^0 = \frac{b+e+h}{3} \qquad \beta_{12}^0 = \frac{c+f+k}{3}$$

$$\beta_1^1 = \frac{g-a}{2} \qquad \beta_2^1 = \frac{h-b}{2} \qquad \beta_{12}^1 = \frac{k-c}{2}$$

$$\beta_1^2 = \frac{g+a-2d}{6} \qquad \beta_2^2 = \frac{h+b-2e}{6} \qquad \beta_{12}^2 = \frac{k+c-2f}{6} .$$

The β_1^0, β_2^0, and β_{12}^0 coefficients now measure the linear and nonlinear component blending properties averaged over the three levels of total amount.

Now, consider the special case of the situation given by (B.5) where the components blend nonlinearly (quadratically) at the middle and high levels of A, but linear blending occurs at the low level of A [i.e., c = 0 in (B.5)]. Substituting c = 0 into the solutions (B.7) yields the revised estimates $\beta_{12}^1 = k/2$ and $\beta_{12}^2 = k/2 - f$. Notice that $\beta_{12}^2 = \beta_{12}^1 - \beta_{12}^0$. Hence, the appropriate mixture-amount model for this situation is of the form (B.6), where $\beta_{12}^2 = \beta_{12}^1 - \beta_{12}^0$.

Next, consider the situation where the components blend nonlinearly (quadratically) at the low and high levels of A, but linear blending occurs at the middle level of A [i.e., f = 0 in (B.5)]. Substituting f = 0 into the solutions

(B.7) yields the revised estimates $\beta_{12}^{0} = 0$ and $\beta_{12}^{2} = (k+c)/2$. Hence, the appropriate mixture-amount model for this situation is of the form (B.6), where $\beta_{12}^{0} = 0$.

Finally, if the components blend nonlinearly (quadratically) at the low and middle levels of A, but linear blending occurs at the high level of A, the appropriate mixture-amount model is of the form (B.6), where $\beta_{12}^{2} = -(\beta_{12}^{0} + \beta_{12}^{1})$. This result is seen by substituting $k = 0$ in (B.7).

B.3 Linear, Linear, and Quadratic Blending at Three Amounts

There are three possibilities to consider here, depending on whether the nonlinear (quadratic) component blending occurs at the low, middle, or high level of A. The parameter estimates for each situation may be obtained from (B.7) by setting the correct pair of values among c, f, and k equal to zero. The appropriate mixture-amount model for each of the three situations is of the form (B.6) with the necessary parameter restrictions as given below.

Quadratic Blending at What Level of A?	Which c, f,k = 0?	Mixture-Amount Model Parameter Restrictions
low level ($A' = -1$)	f,k	$\beta_{12}^{0} = 0$, $\beta_{12}^{2} = -\beta_{12}^{1}$
middle level ($A' = 0$)	c,k	$\beta_{12}^{1} = 0$, $\beta_{12}^{2} = -\beta_{12}^{0}$
high level ($A' = +1$)	c,f	$\beta_{12}^{0} = 0$, $\beta_{12}^{2} = \beta_{12}^{1}$

B.4 Special-Cubic Blending

The special-cubic canonical polynomial mixture model is discussed in Section 2.1. Situations in which special-cubic blending occurs at one of two levels of A are now considered. For simplicity, only three-component mixture-amount experiments are considered here. The results readily extend to $q > 3$ components.

It will be helpful to consider the general situation for three components,

$$\eta_{A'=-1} = \sum_{i=1}^{3} b_i x_i + \sum_{i<j}^{3} \sum b_{ij} x_i x_j + b_{123} x_1 x_2 x_3$$

$$\eta_{A'=+1} = \sum_{i=1}^{3} c_i x_i + \sum_{i<j}^{3} \sum c_{ij} x_i x_j + c_{123} x_1 x_2 x_3 , \qquad (B.8)$$

where the two levels of A are coded as -1 and +1. The notation A' is used to denote the coded version of the total amount variable A. The appropriate mixture-amount model for this general situation is

$$\eta = \sum_{h=0}^{1} \left[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \sum \beta_{ij}^h x_i x_j + \beta_{123}^h x_1 x_2 x_3 \right] (A')^h . \qquad (B.9)$$

The unique solutions for the parameters are given by

$$\beta_i^0 = \frac{b_i+c_i}{2} \qquad i=1,2,3 \qquad\qquad \beta_i^1 = \frac{c_i-b_i}{2} \qquad i=1,2,3$$

$$\beta_{ij}^0 = \frac{b_{ij}+c_{ij}}{2} \qquad 1\leq i<j\leq 3 \qquad\qquad \beta_{ij}^1 = \frac{c_{ij}-b_{ij}}{2} \qquad 1\leq i<j\leq 3$$

$$\beta_{123}^0 = \frac{b_{123}+c_{123}}{2} \qquad\qquad \beta_{123}^1 = \frac{c_{123}-b_{123}}{2} \qquad\qquad (B.10)$$

The appropriate parameter restrictions on (B.9) for several situations are given in Table B.1.

Although not presented here, one can easily develop the mixture-amount model parameter restrictions for various situations with special-cubic blending when A takes on three levels.

Table B.1. Parameter Restrictions with Special Cubic Blending

Type Blending		Individual Model Restrictions in (B.8)	Mixture-Amount Model Parameter Restrictions
$A' = -1$	$A' = +1$		
linear	special-cubic	$b_{12} = b_{13} = b_{23} = b_{123} = 0$	$\beta^1_{ij} = \beta^0_{ij}$ $1 \leq i < j \leq 3$; $\beta^1_{123} = \beta^0_{123}$
special-cubic	linear	$c_{12} = c_{13} = c_{23} = c_{123} = 0$	$\beta^1_{ij} = -\beta^0_{ij}$ $1 \leq i < j \leq 3$; $\beta^1_{123} = -\beta^0_{123}$
quadratic	special-cubic	$b_{123} = 0$	$\beta^1_{123} = \beta^0_{123}$
special-cubic	quadratic	$c_{123} = 0$	$\beta^1_{123} = -\beta^0_{123}$

APPENDIX C
THREE COMPONENT D_N-OPTIMAL DESIGNS FOR VARIOUS CANONICAL POLYNOMIAL MIXTURE-AMOUNT MODELS

Several D_N-optimal designs for various Scheffé canonical polynomial mixture-amount models are displayed graphically in this appendix. The designs are for mixture-amount experiments with $q = 3$ components and $r = 2$ or 3 levels of amount. The designs were obtained using the DETMAX program of Mitchell (1974), and are D_N-optimal for most of the models we consider. The designs that are not D_N-optimal are very nearly so.

Designs are displayed for a range of N values for each model. For most values of N, there are many possible D_N-optimal designs; we show three designs for the cases with $r = 2$ and two designs for the cases with $r = 3$. In cases where only one or two unique designs or patterns exist, a note to that effect is given.

The values of N selected for each model range from p to C+p, where p is the number of parameters in the model and C is the number of candidate points for the design. For each of the nine models in the following sections, the $N = C+p$ designs consist of the C candidate points plus one of the

$N = p$ designs. Hence, designs for $N \geq C+p$ follow directly from those for $p \leq N < C+p$.

The results in the following sections for $q = 3$ suggest general procedures for generating D_N-optimal designs for all values of $q \geq 3$. These procedures are given in Tables 4.4 - 4.12 of Chapter 4.

C.1 Two Levels of Amount

Several D_N-optimal designs for mixture-amount experiments with $q = 3$ and $r = 2$ were obtained using DETMAX. Designs for several values of N for each of six different canonical polynomial mixture-amount models are displayed in Figures C.1 - C.6. The candidate points for the designs in Figures C.1 - C.3 and Figures C.4 - C.6 are given respectively in Tables C.1 and C.2.

For a given design displayed in Figures C.1 - C.6, note that the two simplexes have not been labeled as to which is the low level of A (coded as $A' = -1$) and which is the high level (coded as $A' = +1$). Similarly, the individual simplexes have not been labeled as to which vertex represents which pure component. The designs displayed in Figures C.1 - C.6 are D_N-optimal regardless of how the simplexes are labeled; that is, either one of a pair of simplexes may be labeled as the low level of amount and the other as the high level, while any component labeling is alright (as long as both simplexes of a pair are labeled the same).

The D_N-optimal designs in Figures C.1 - C.6 are laid out so that the designs (consisting of a pair of simplexes) in each of the three design columns form a sequence of D_N-optimal designs. That is, each design in the figures is D_N-optimal and is obtainable by adding the appropriate number of new points to the D_N-optimal design directly above it.

Finally, as a point of interest, for $N \geq 12$ the designs in Figures C.1 and C.2 are also D_N-optimal for the model of Figure C.3. Also, for $N \geq 14$, the designs in Figures C.4 and C.5 are also D_N-optimal for the model of Figure C.6. Unfortunately, the designs of Figure C.1 (alternately C.4) are usually not D_N-optimal for the model of Figure C.2 (alternately C.5), nor are the designs of Figure C.2 (alternately C.5) usually D_N-optimal for the model of Figure C.1 (alternately C.4).

The observations and comments made in the previous two paragraphs are discussed further for $q \geq 3$ in Section 4.2 of Chapter 4.

C.2 Three Levels of Amount

The DETMAX program was used to generate designs for unconstrained mixture-amount experiments with $q = 3$ and $r = 3$. Designs for several values of N for each of three canonical polynomial mixture-amount models are displayed in Figures C.7 - C.9. The designs in Figure C.9 are D_N-optimal for the corresponding model, while the designs in Figures

C.7 and C.8 are D_N-optimal or nearly D_N-optimal. The candidate points for the designs in Figures C.7 - C.9 are given in Table C.3.

For a given design (consisting of three simplexes) in Figures C.7 - C.9, note that the three simplexes have not been labeled as to which ones are associated with the three levels of A (assumed to be coded as $A' = -1, 0, +1$), nor have the individual simplexes been labeled as to which vertex represents which pure component. The middle simplex of the three for a given design is taken to be at $A' = 0$, while the two outside simplexes may be associated with $A' = -1$ and $A' = +1$ in either order. The vertices may be associated with the pure components in any way, as long as the labeling is the same for each of the three simplexes of a given design. Within these limitations, any design obtained through a particular labeling is D_N-optimal (or nearly so).

The D_N-optimal designs in Figures C.7 and C.9 (actually near D_N-optimal in the case of some Figure C.7 designs) are laid out so that the designs in each design column form a sequence of D_N-optimal designs. That is, each design in the figures is D_N-optimal and is obtainable by adding the appropriate number of new points to the D_N-optimal design directly above it. Because of the nature of the associated mixture-amount model, it was not possible to arrange the designs in Figure C.8 to satisfy this sequential property

for all values of N considered. It is possible for $15 \leq N \leq 24$ (both columns in Figure C.8) and for $25 \leq N \leq 32$ (the first column of designs), but the $25 \leq N \leq 32$ designs are not obtainable from the unique N = 24 design.

Finally, it is interesting to note that for $N \geq 18$ the designs in Figures C.7 and C.8 are also D_N-optimal (or nearly so) for the model of Figure C.9. This comment is discussed further in Section 4.2 of Chapter 4.

Table C.1. Candidate Points for Mixture-Amount Models With Quadratic Blending and Two Levels of A

x_1	x_2	x_3	A'
1	0	0	-1
0	1	0	-1
0	0	1	-1
1/2	1/2	0	-1
1/2	0	1/2	-1
0	1/2	1/2	-1
1	0	0	1
0	1	0	1
0	0	1	1
1/2	1/2	0	1
1/2	0	1/2	1
0	1/2	1/2	1

Table C.2. Candidate Points for Mixture-Amount Models With Special-Cubic Blending and Two Levels of A

x_1	x_2	x_3	A'
1	0	0	-1
0	1	0	-1
0	0	1	-1
1/2	1/2	0	-1
1/2	0	1/2	-1
0	1/2	1/2	-1
1/3	1/3	1/3	-1
1	0	0	1
0	1	0	1
0	0	1	1
1/2	1/2	0	1
1/2	0	1/2	1
0	1/2	1/2	1
1/3	1/3	1/3	1

Table C.3. Candidate Points for Mixture-Amount Models With Quadratic Blending and Three Levels of A

x_1	x_2	x_3	A'
1	0	0	-1
0	1	0	-1
0	0	1	-1
1/2	1/2	0	-1
1/2	0	1/2	-1
0	1/2	1/2	-1
1	0	0	0
0	1	0	0
0	0	1	0
1/2	1/2	0	0
1/2	0	1/2	0
0	1/2	1/2	0
1	0	0	1
0	1	0	1
0	0	1	1
1/2	1/2	0	1
1/2	0	1/2	1
0	1/2	1/2	1

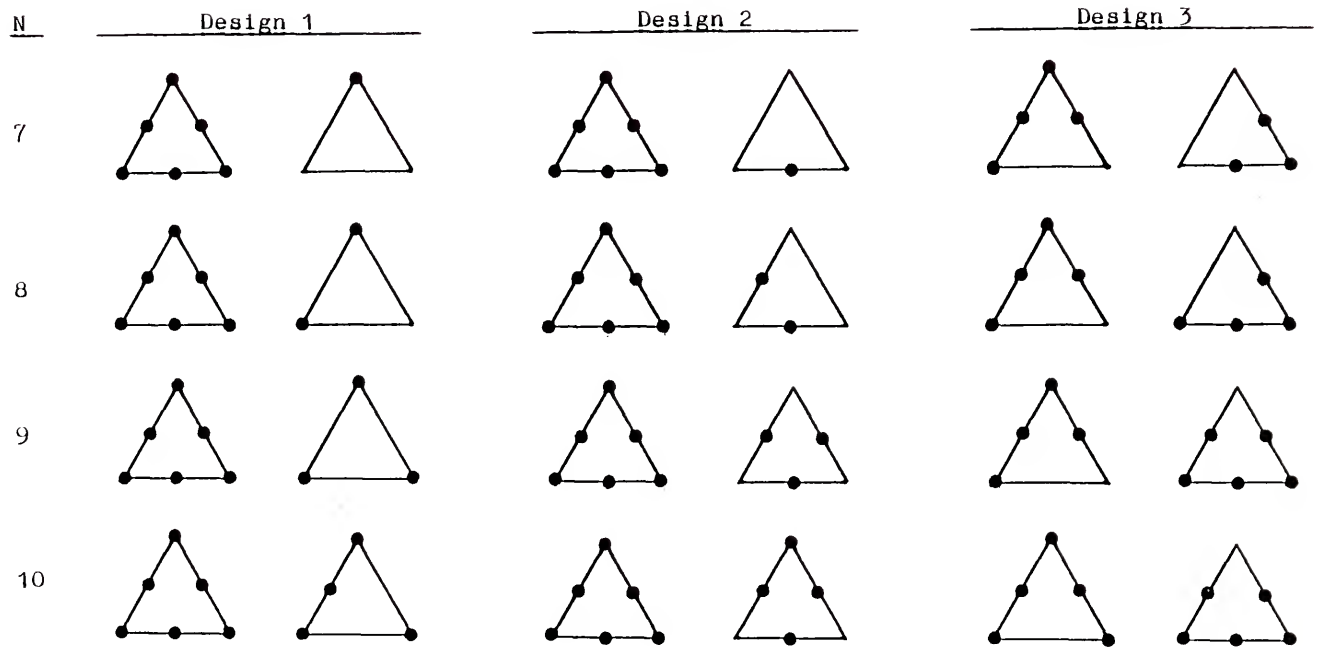


Figure C.1. D_N-Optimal Designs for Two Levels of A and Model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \sum \beta_{ij}^0 x_i x_j + \beta_0^1 A'$$

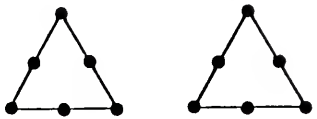
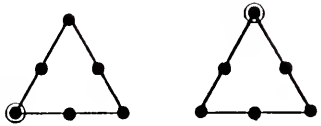
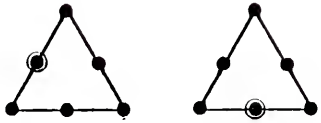
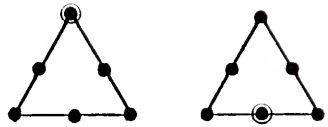
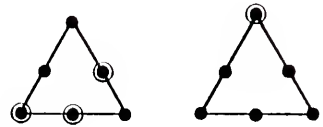
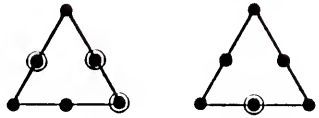
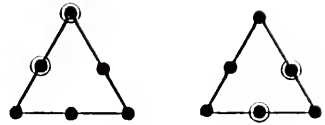
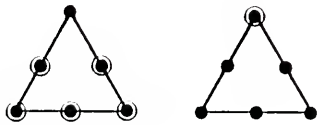
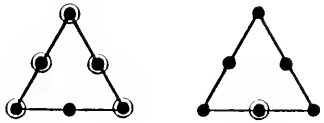
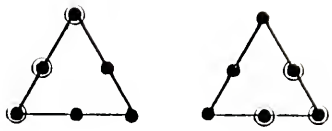
N	Design 1	Design 2	Design 3
12		unique design	unique design
14			
16			
18			

Figure C.1-continued.

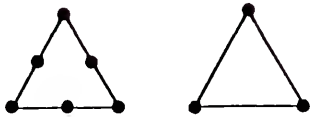
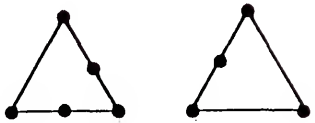
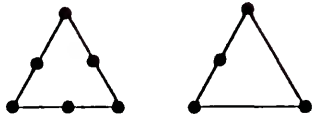
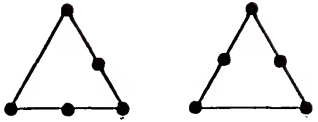
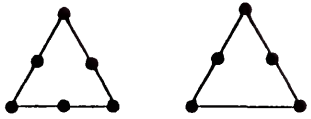
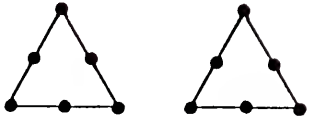
N	Design 1	Design 2	Design 3
9			only two unique patterns
10			only two unique patterns
11		only one unique pattern	only one unique pattern
12		unique design	unique design

Figure C.2. D_N-Optimal Designs for Two Levels of A and Model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \beta_{ij}^0 x_i x_j + \sum_{i=1}^{3} \beta_i^1 x_i A'$$

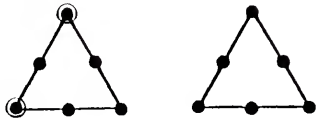
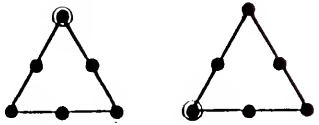
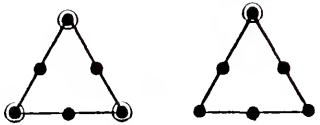
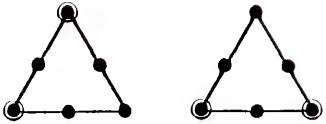
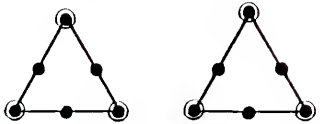
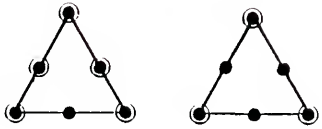
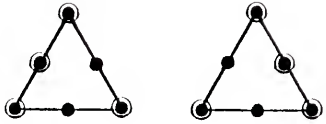
N	Design 1	Design 2	Design 3
14			only two unique patterns
16			only two unique patterns
18		unique design	unique design
20			only two unique patterns

Figure C.2-continued.

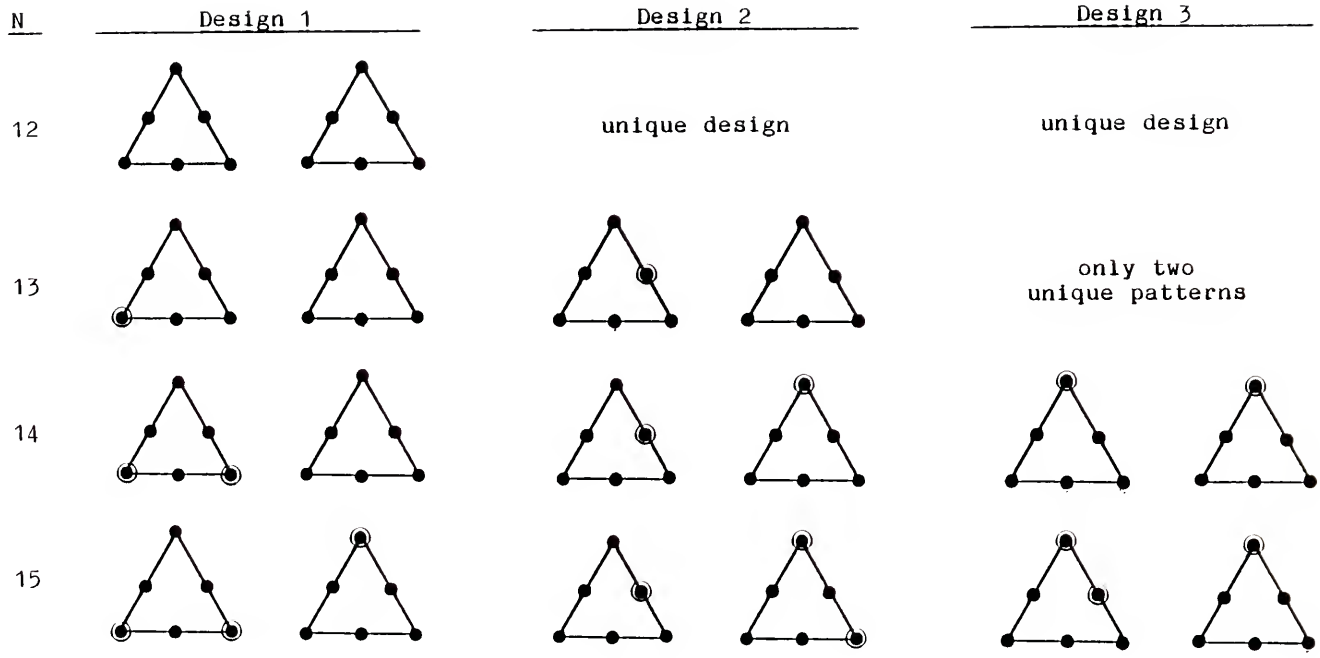


Figure C.3. D_N-Optimal Designs for Two Levels of A and Model

$$\eta = \sum_{h=0}^{1} \left[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \sum \beta_{ij}^h x_i x_j \right] (A')^h$$

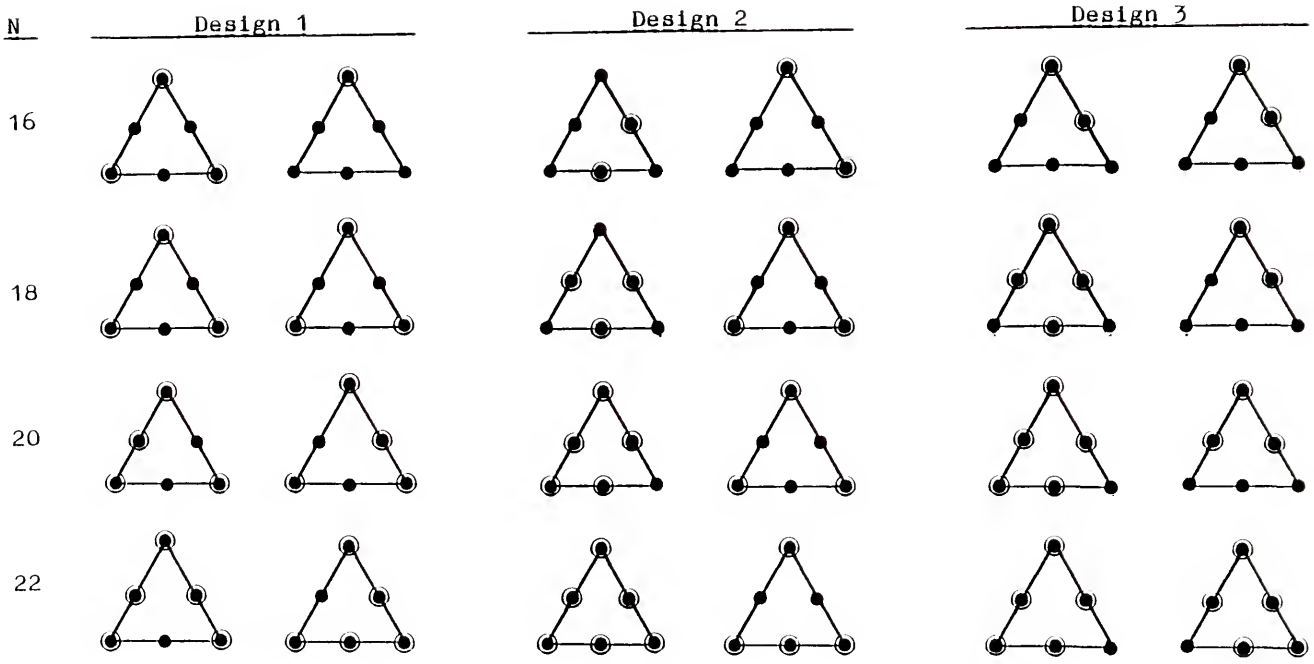


Figure C.3-continued.

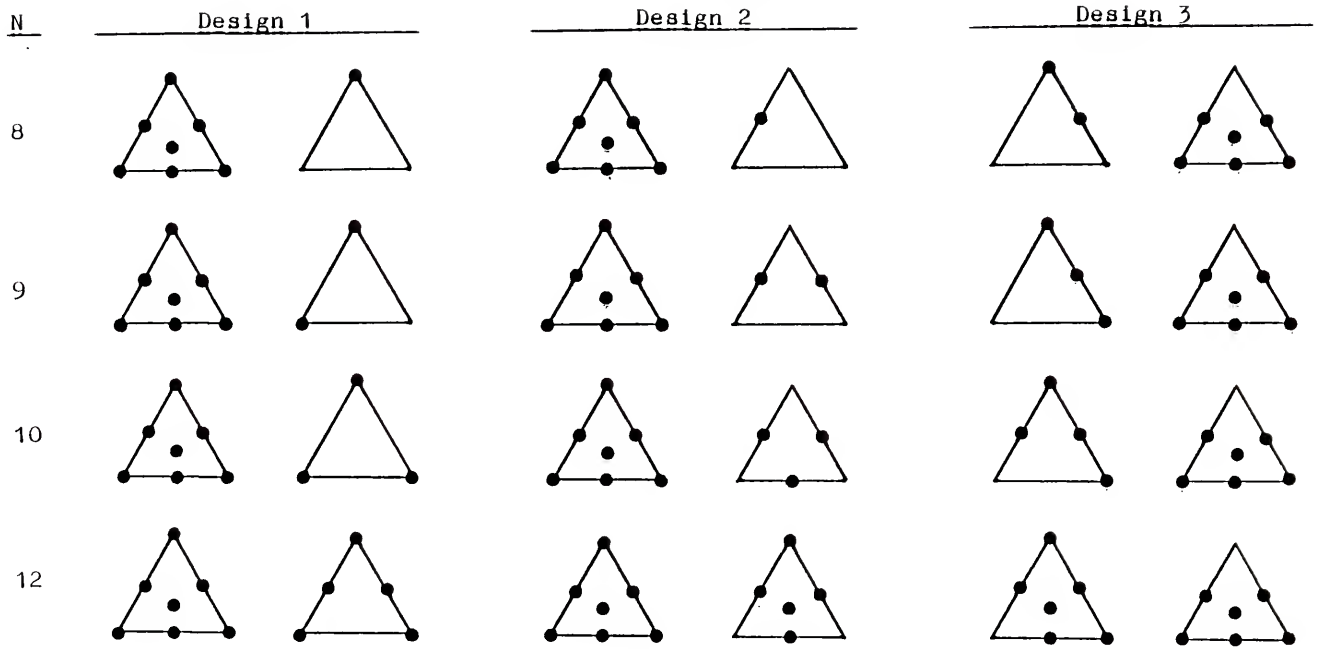


Figure C.4. D_N-Optimal Designs for Two Levels of A and Model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \sum \beta_{ij}^0 x_i x_j + \beta_{123}^0 x_1 x_2 x_3 + \beta_0^1 A'$$

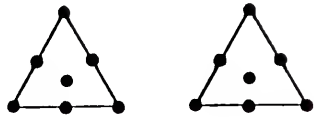
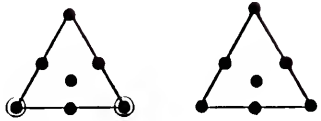
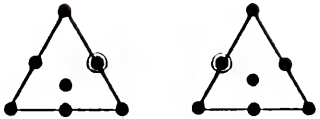
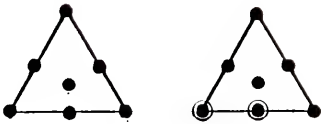
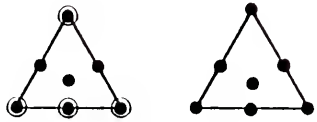
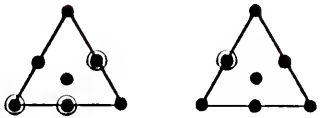
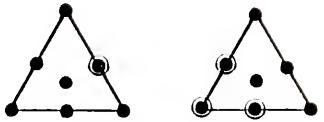
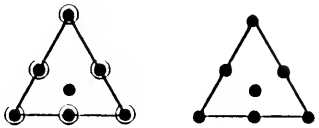
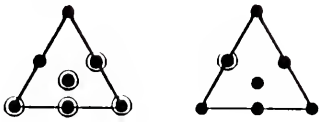
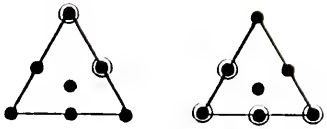
N	Design 1	Design 2	Design 3
14		unique design	unique design
16			
18			
20			

Figure C.4-continued.

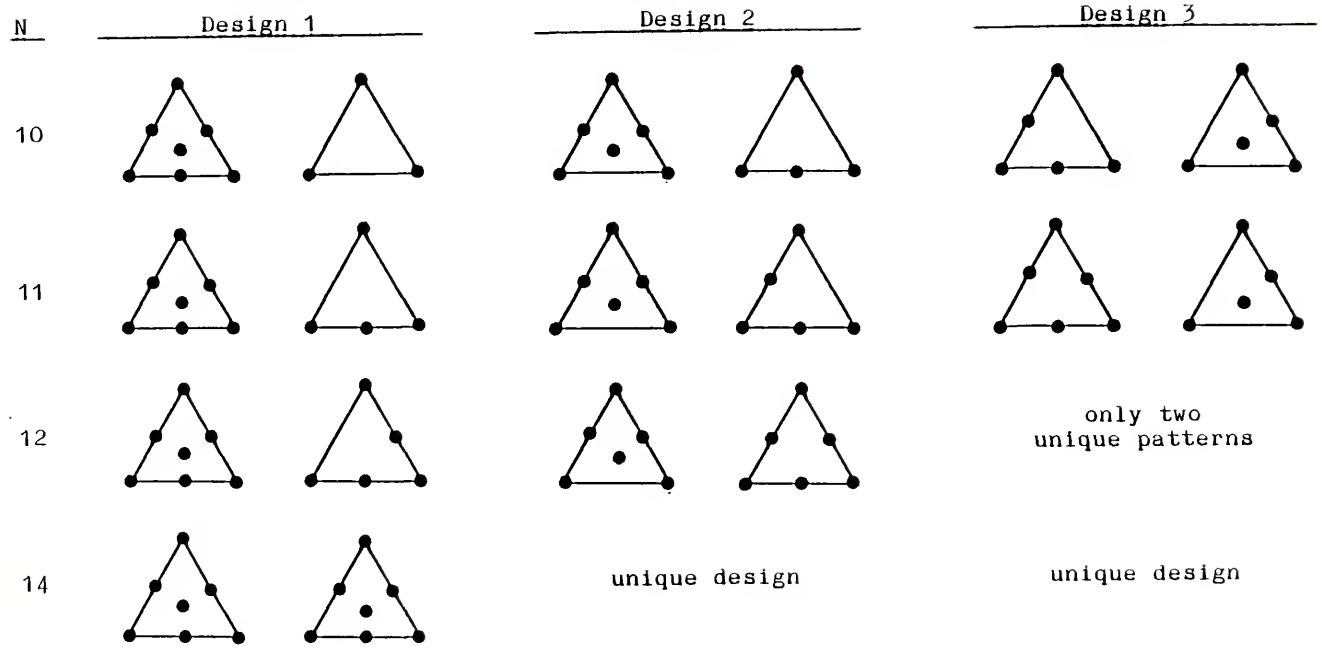


Figure C.5. D_N-Optimal Designs for Two Levels of A and Model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \sum \beta_{ij}^0 x_i x_j + \beta_{123}^0 x_1 x_2 x_3 + \sum_{i=1}^{3} \beta_i^1 x_i A'$$

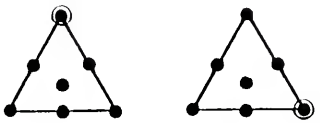
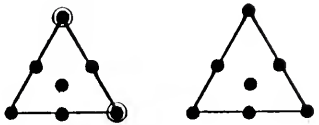
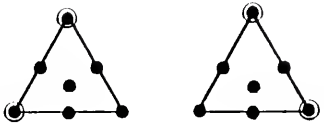
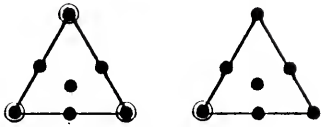
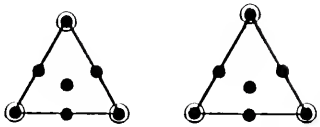
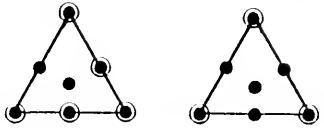
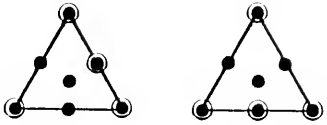
N	Design 1	Design 2	Design 3
16			only two unique patterns
18			only two unique patterns
20		unique design	unique design
22			only two unique patterns

Figure C.5-continued.

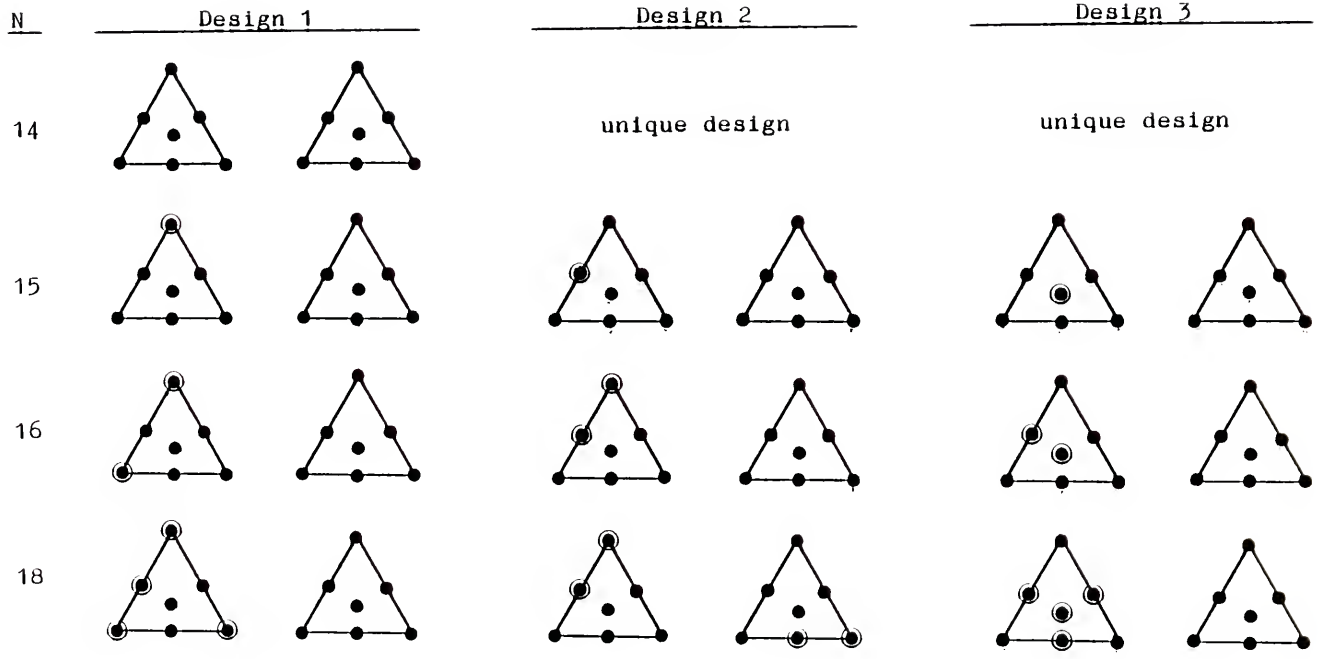


Figure C.6. D_N-Optimal Designs for Two Levels of A and Model

$$\eta = \sum_{h=0}^{1} \left[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \beta_{ij}^h x_i x_j + \beta_{123}^h x_1 x_2 x_3 \right] (A')^h$$

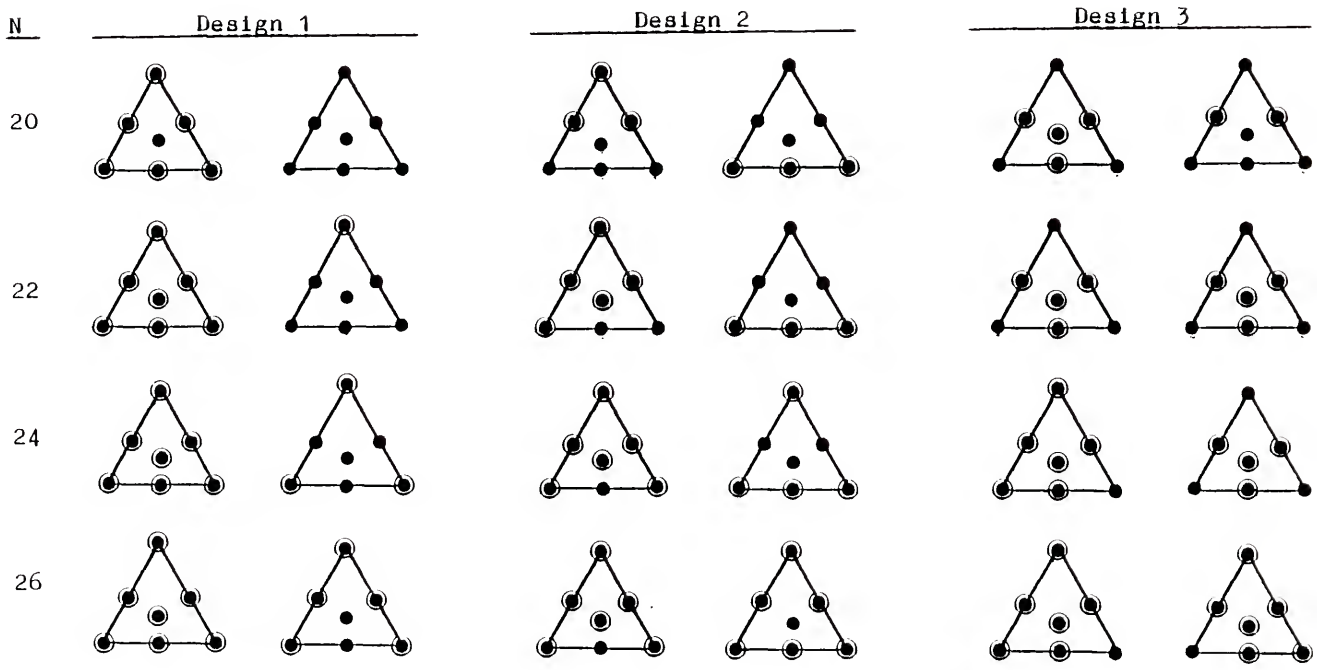


Figure C.6-continued.

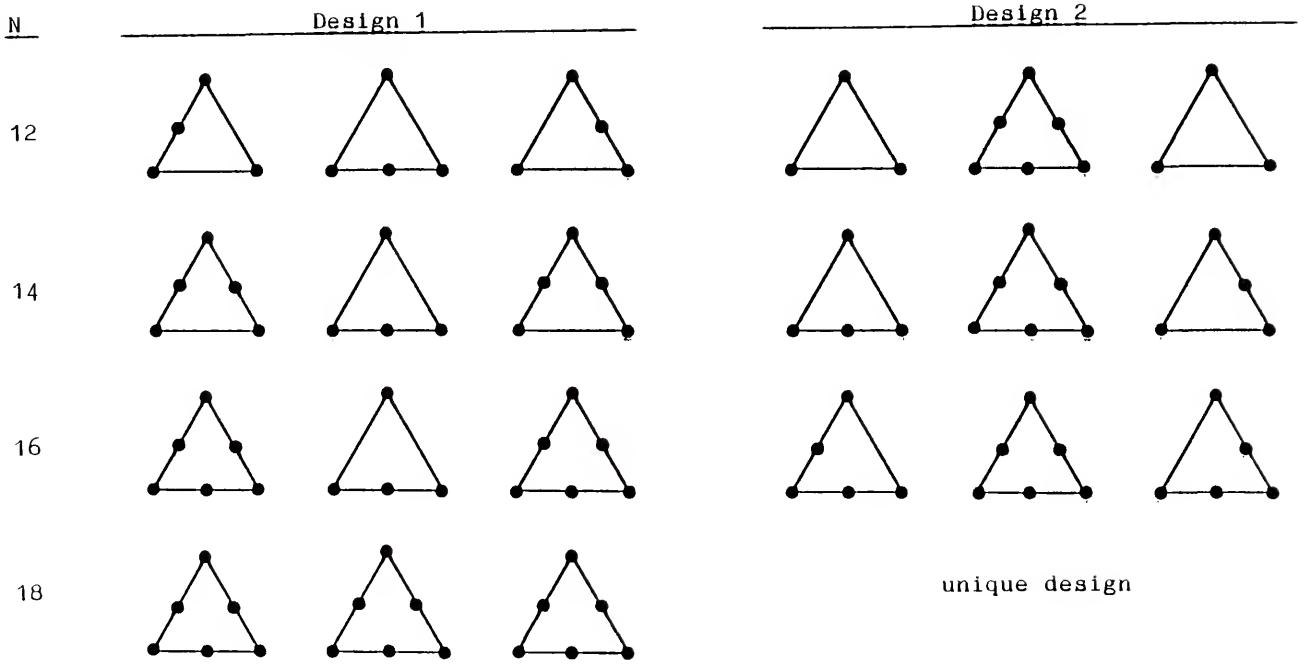


Figure C.7. D_N-Optimal or Near D_N-Optimal Designs for Three Levels of A and Model

$$\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \sum \beta_{ij}^0 x_i x_j + \sum_{i=1}^{3} \beta_i^1 x_i A' + \sum_{i=1}^{3} \beta_i^2 x_i (A')^2$$

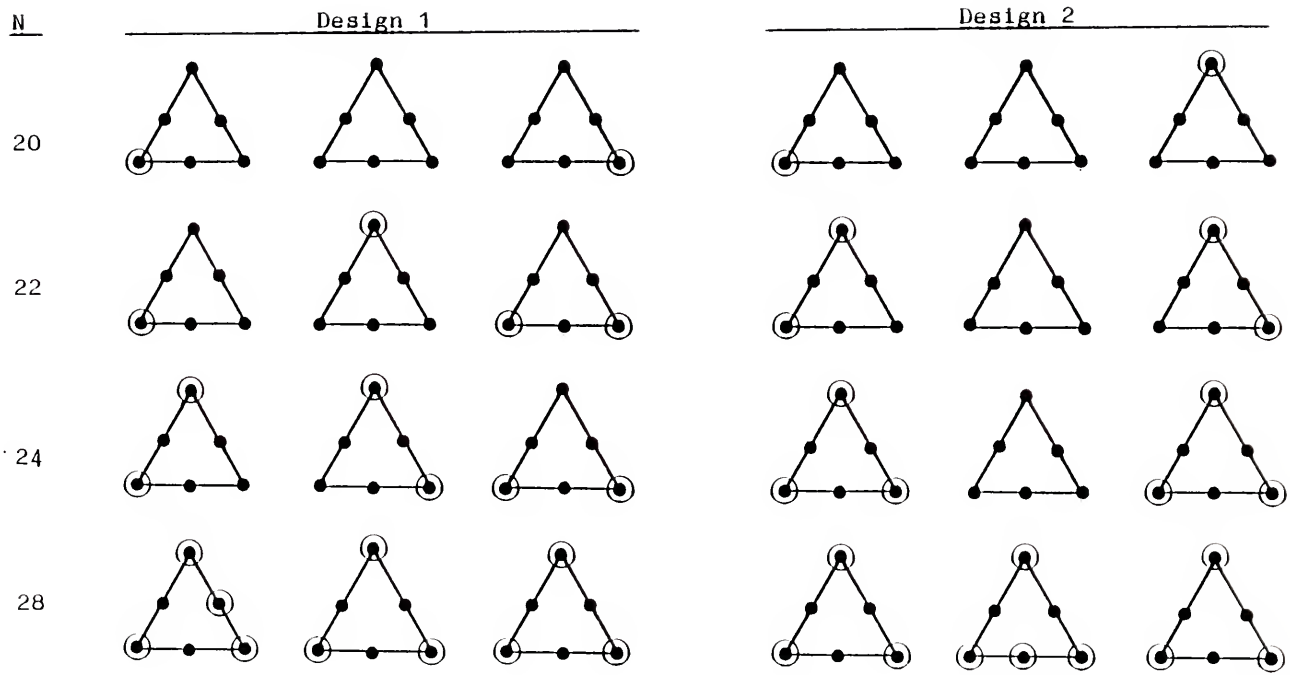


Figure C.7-continued.

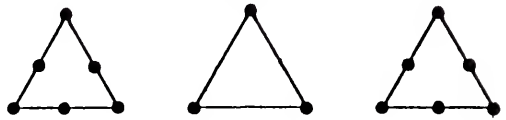
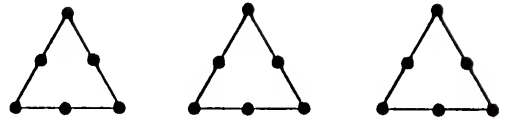
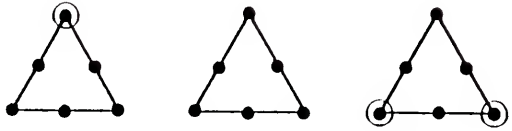
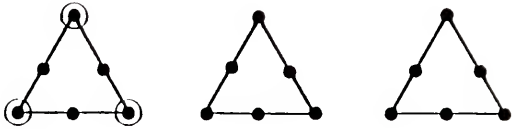
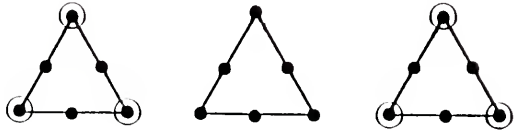
N	Design 1	Design 2
15		unique design
18		unique design
21		
24		unique design

Figure C.8. D_N-Optimal or Near D_N-Optimal Designs for Three Levels of A and Model

$$\eta = \sum_{h=0}^{1} \left[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \beta_{ij}^h x_i x_j \right] (A')^h + \sum_{i=1}^{3} \beta_i^2 x_i (A')^2$$

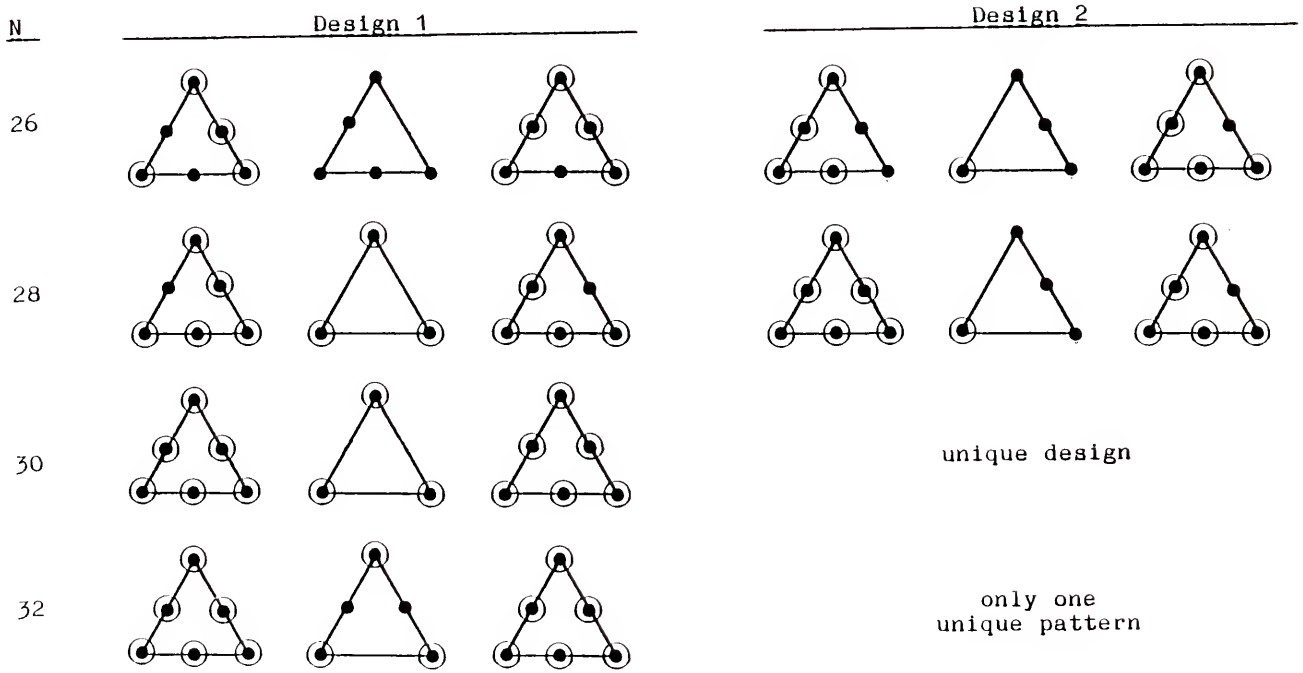


Figure C.8-continued.

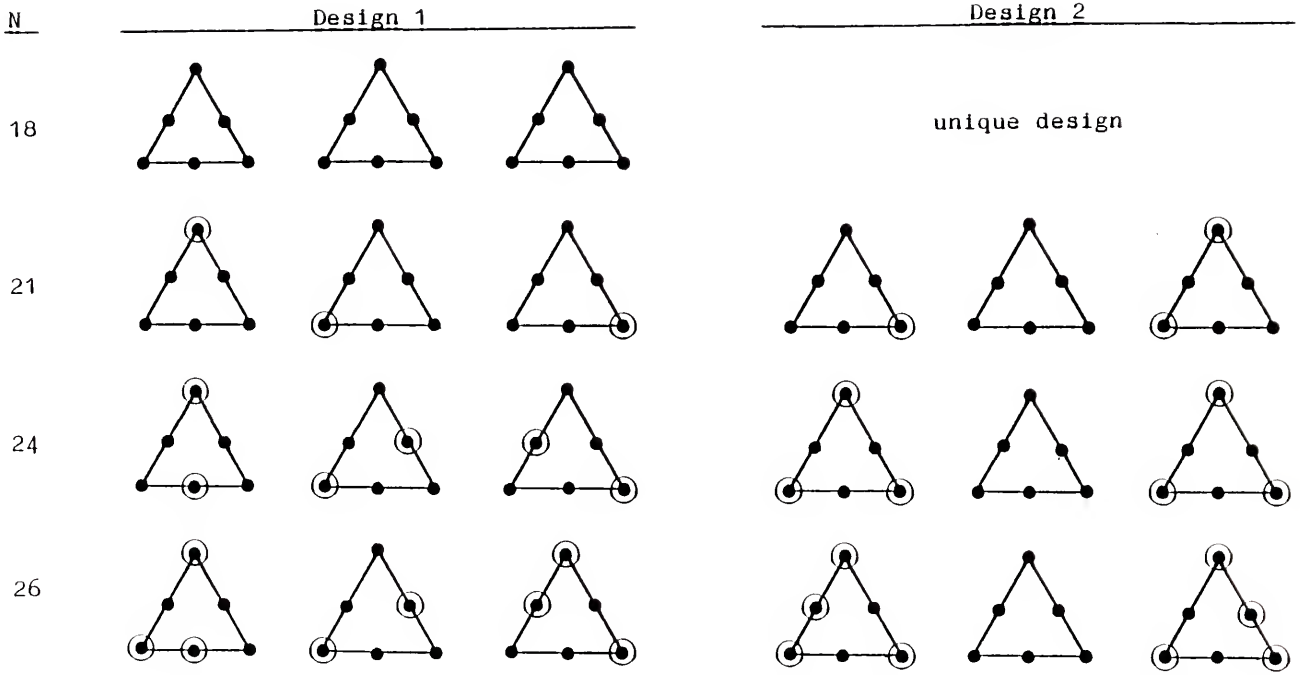


Figure C.9. D_N-Optimal Designs for Three Levels of A and Model

$$\eta = \sum_{h=0}^{2} \left[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \sum \beta_{ij}^h x_i x_j \right] (A')^h$$

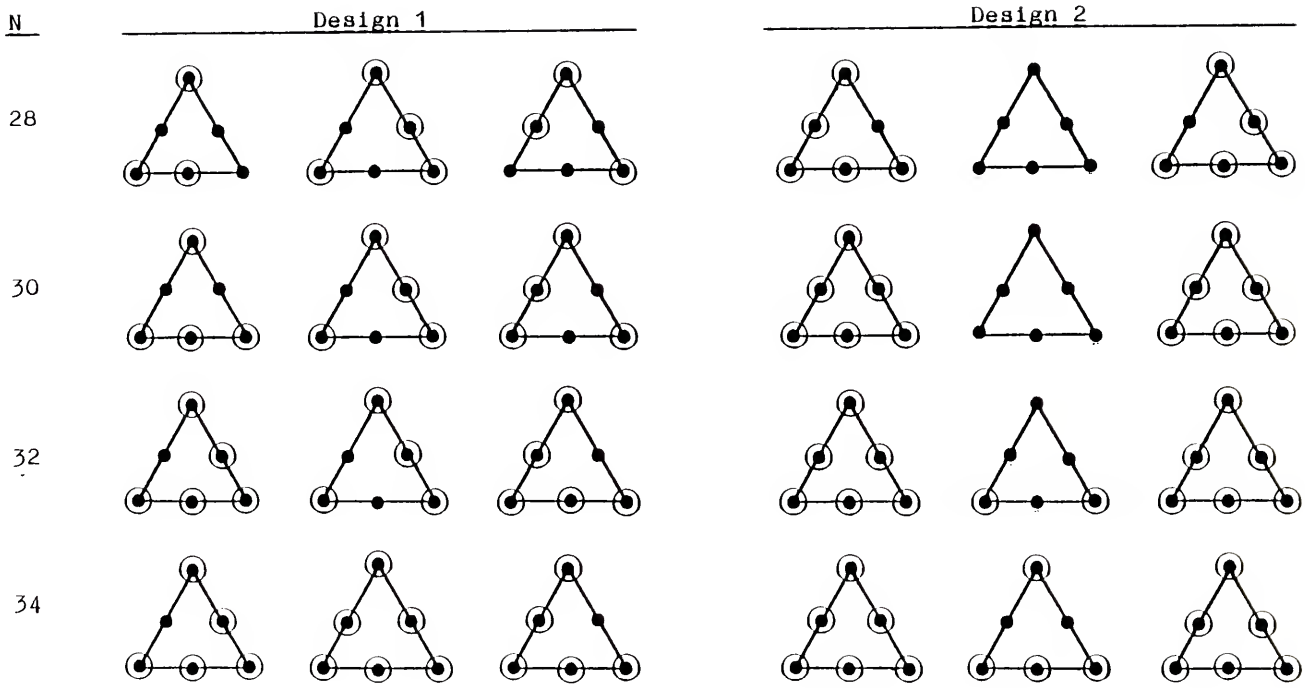


Figure C.9-continued.

APPENDIX D
CONSIDERATIONS IN CHOOSING AMONG TWO OR MORE D_N-OPTIMAL DESIGNS

It is clear from the designs displayed in Figures C.1 - C.9 in Appendix C, that for a given model and value of N, there is often more than one D_N-optimal design. We now discuss other design characteristics and properties that can be used to select a particular design from a group of D_N-optimal designs.

D.1 Other Optimality Criteria and Parameter Variances

We used the D_N-optimality criterion in Chapter 4 in applying a computer-aided design approach to fractionate mixture-amount designs. To select a particular design from a group of several D_N-optimal designs, other common optimality criteria such as A_N, G_N, and V_N-optimality can be used. These criteria are based on the design measures $tr[(X'X)^{-1}]$, max d, and avg d, respectively, where $d = \underset{\sim}{x}'(X'X)^{-1}\underset{\sim}{x}$ and the maximum or average is computed over the set of candidate points. The elements of the vector $\underset{\sim}{x}$ are the coordinates as well as functions of the coordinates (as determined by the form of the mixture-amount model) of each point in the set of candidate points.

The values of max d and avg d are often the same for each D_N-optimal design for a given model and value of N. This is the case for most values of N in Figures C.1 - C.6 in Appendix C. However, usually the value of $tr[(X'X)^{-1}]$ will not be the same for all D_N-optimal designs for a given model and value of N. As an example, consider the following values of the three measures calculated from designs 1 and 2 in Figure C.3 for the case N = 18.

	Design 1	Design 2
$tr[(X'X)^{-1}]$	61.50	56.25
max d	1.00	1.00
avg d	0.75	0.75

The trace measure is the only one of the three criteria that provides any discrimination between the two designs. Since $tr[(X'X)^{-1}]$ is proportional to the sum of the variances of the parameter estimates, a small value is desirable. Based on this criterion, we would prefer design 2 over design 1.

In trying to choose one among several D_N-optimal designs, it is sometimes helpful to consider criteria which provide information about the individual parameter estimates in the fitted model. For example, the individual diagonal elements of the matrix $(X'X)^{-1}$ are proportional to the variances of the individual parameter estimates in the fitted model (recall from equation (1.5) that

$\text{Var}(\hat{\underset{\sim}{\beta}}) = (X'X)^{-1}\sigma^2)$. For simplicity, in this appendix we will refer to the diagonal elements of $(X'X)^{-1}$ as the variances of the parameter estimates for the purpose of comparing designs. These variances for the two N = 18 designs from Figure C.3 are given by

Parameter in the Model	Var(Parameter Estimate)/σ^2	
	Design 1	Design 2
β_1^0	.25	.375
β_2^0	.25	.375
β_3^0	.25	.375
β_{12}^0	10.00	9.000
β_{13}^0	10.00	9.000
β_{23}^0	10.00	9.000
β_1^1	.25	.375
β_2^1	.25	.375
β_3^1	.25	.375
β_{12}^1	10.00	9.000
β_{13}^1	10.00	9.000
β_{23}^1	10.00	9.000

If an experimenter is interested primarily in the linear blending properties of the components as well as the effect of the total amount of the mixture on the linear blending

properties, he would select design 1. On the other hand, if the experimenter expects that the nonlinear component blending effects will be large and that they will be affected by the level of total amount, he might select design 2 rather than design 1.

We now consider an example from Appendix C where the designs obtained using DETMAX are only near D_N-optimal. Specifically, consider the two designs given in Figure C.7 for the case N = 24. The values of $\det(X'X)$, $\mathrm{tr}[(X'X)^{-1}]$, max d, avg d, and the $(1/\sigma^2)\mathrm{Var}(\hat{\beta}_k)$ are given in Table D.1. Design 1 gives a slightly larger value of $\det(X'X)$ and slightly smaller values of the other three measures than does design 2, and hence might be preferred. Design 1 yields considerably smaller variances for $\hat{\beta}^0_1$, $\hat{\beta}^0_3$, $\hat{\beta}^2_1$, and $\hat{\beta}^2_3$, and somewhat larger variances for $\hat{\beta}^1_1$ and $\hat{\beta}^1_3$ than does design 2. If we base our choice of design on the magnitudes of the variances of the parameter estimates, and select the design that provides the greater number of estimates with lower variances, then design 1 appears to be slightly better than design 2.

D.2 Parameter Estimates as Functions of the Observations

It may also be helpful in choosing among several D_N-optimal designs to consider how the parameter estimates are expressible as functions of the observations y_i, i=1,2, . . . ,N, at points of the design. To help illustrate how

Table D.1. Design Criteria Values and Parameter Variances for Two N = 24 Designs from Figure C.7

	Design 1	Design 2
$\det(X'X)$	137.78	137.21
$\mathrm{tr}[(X'X)^{-1}]$	25.923	26.865
max d	0.7820	0.7868
avg d	0.5196	0.5198

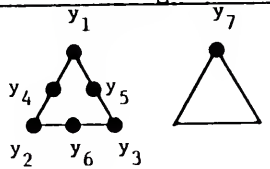
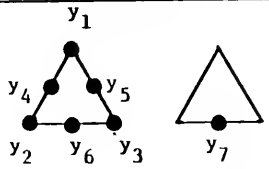
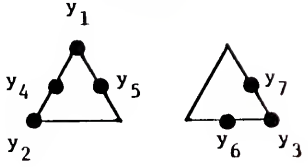
Parameter Estimate	Var(Parameter Estimate)/σ^2 Design 1	Design 2
$\hat{\beta}^0_1$	.441	.787
$\hat{\beta}^0_2$	.782	.787
$\hat{\beta}^0_3$	.441	.787
$\hat{\beta}^0_{12}$	7.071	7.047
$\hat{\beta}^0_{13}$	7.071	7.047
$\hat{\beta}^0_{23}$	7.071	7.047
$\hat{\beta}^1_1$	.278	.204
$\hat{\beta}^1_2$	.205	.204
$\hat{\beta}^1_3$	.278	.204
$\hat{\beta}^2_1$	.688	.917
$\hat{\beta}^2_2$	.909	.917
$\hat{\beta}^2_3$	.688	.917

this information might be used to select a design from among two or more D_N-optimal designs, consider designs 1, 2, and 3 from Table C.1 in Appendix C for the case N = 7. The formulas for the parameter estimates in terms of the observations collected at the design points are given in Table D.2. The designs are displayed again in Table D.2 to aid in the discussion.

Each of the three designs covers the six positions once, with one position covered twice (once at each of the two levels of A, coded as -1 and +1). As is expected with each of the three designs, β_0^1 (the effect of A) is estimated by one-half the difference between the observed response values at the position covered at each of the two levels of A. Because of the assumed form of the model (given at the top of Table D.2), the effect of total amount is assumed to be the same at every blend (i.e., the total amount does not affect the component blending). This amount effect is contained in the estimates of some of the parameters with all three designs. For design 2, the amount effect enters the estimates $\hat{\beta}_1^0$, $\hat{\beta}_2^0$, and $\hat{\beta}_3^0$ directly in that $\hat{\beta}_i^0 = y_i + \hat{\beta}_0^1$ (as seen in Table D.2). The $\hat{\beta}_{12}^0$, $\hat{\beta}_{13}^0$, and $\hat{\beta}_{23}^0$ for design 2 are actually the estimates of the nonlinear component blending properties at the lower level of A. However, since the model imposes the assumption that the total amount does not affect the component blending properties, the estimates are assumed to be appropriate at both levels of A.

Table D.2. Parameter Estimates as Functions of the Observations at the Data Points

Model: $\eta = \sum_{i=1}^{3} \beta_i^0 x_i + \sum_{i<j}^{3} \sum \beta_{ij}^0 x_i x_j + \beta_0^1 A'$

	Design 1	Design 2	Design 3
	 A' = -1 A' = +1	 A' = -1 A' = +1	 A' = -1 A' = +1
$\hat{\beta}_1^0$	$(y_1+y_7)/2$	$y_1 + (y_7-y_6)/2$	$y_1 + (y_7-y_5)/2$
$\hat{\beta}_2^0$	$y_2 + (y_7-y_1)/2$	$y_2 + (y_7-y_6)/2$	$y_2 + (y_7-y_5)/2$
$\hat{\beta}_3^0$	$y_3 + (y_7-y_1)/2$	$y_3 + (y_7-y_6)/2$	$y_3 + (y_7-y_5)/2$
$\hat{\beta}_{12}^0$	$4y_4 - 2y_1 - 2y_2$	$4y_4 - 2y_1 - 2y_2$	$4y_4 - 2y_1 - 2y_2$
$\hat{\beta}_{13}^0$	$4y_5 - 2y_1 - 2y_3$	$4y_5 - 2y_1 - 2y_3$	$2y_5+2y_7-2y_1-2y_3$
$\hat{\beta}_{23}^0$	$4y_6 - 2y_2 - 2y_3$	$4y_6 - 2y_2 - 2y_3$	$4y_6-2y_2-2y_3-2y_7+2y_5$
$\hat{\beta}_0^1$	$(y_7 - y_1)/2$	$(y_7 - y_6)/2$	$(y_7 - y_5)/2$

The situation for design 1 is almost the same as for design 2, except that $\hat{\beta}^{0}_{1}$ does not depend on the assumed model. For design 3, the results are similar to those for design 2, except that $\hat{\beta}^{0}_{13}$ and $\hat{\beta}^{0}_{23}$ depend directly on the assumed model and are not computed based totally on observations taken at one of the two levels of amount (as is the case for both designs 1 and 2).

It has been instructive in this example to express the parameter estimates as linear functions of the observations at the design points with each design, and to consider how the form of the assumed model affects these estimates. We can extend these investigations somewhat by looking at the bias in the parameter estimates under different "true" model forms. To illustrate this, recall for our example that the three designs under consideration for the case N = 7 were developed for the model

$$\eta = \sum_{i=1}^{3} \beta^{0}_{i} x_i + \sum_{i<j}^{3} \sum \beta^{0}_{ij} x_i x_j + \beta^{1}_{0} A' \ . \qquad (D.1)$$

However, if

$$\eta = \sum_{i=1}^{3} \beta^{0}_{i} x_i + \sum_{i<j}^{3} \sum \beta^{0}_{ij} x_i x_j + \sum_{i=1}^{3} \beta^{1}_{i} x_i A' \qquad (D.2)$$

is the true form of the model, then certain parameter estimates given in Table D.2 will be biased. The expectations of the parameter estimates in Table D.2,

assuming equation (D.2) is the true underlying model, are given in Table D.3. The nonlinear blending parameter estimates $\hat{\beta}^0_{12}$, $\hat{\beta}^0_{13}$, and $\hat{\beta}^0_{23}$ are all unbiased for designs 1 and 2, whereas only $\hat{\beta}^0_{12}$ is unbiased for design 3. The linear blending parameter estimates $\hat{\beta}^0_1$, $\hat{\beta}^0_2$, and $\hat{\beta}^0_3$ are biased for all three designs (with the exception of $\hat{\beta}^0_1$ in design 1, which is unbiased).

To summarize, if the property of unbiasedness of the parameter estimates is desired, then design 1 appears to be preferable to designs 2 and 3 since a greater number of the parameter estimates in the fitted model (D.1) are unbiased with design 1. Even if the assumed model (D.1) is not correct, the parameters in the mixture-only model can be estimated cleanly with both designs 1 and 2, since with each design a complete lattice arrangement is set up at the low level of A. Under the true model (D.2), designs 1 and 2 provide unbiased estimates of β^0_{12}, β^0_{13}, and β^0_{23}, but only with design 1 is $\hat{\beta}^0_1$ an unbiased estimate of β^0_1 under the model (D.2), or even under the model

$$\eta = \sum_{h=0}^{1} \Big[\sum_{i=1}^{3} \beta_i^h x_i + \sum_{i<j}^{3} \sum \beta_{ij}^h x_i x_j \Big] (A')^h \ . \qquad (D.3)$$

The techniques used in the example above are completely general and may be used to compare two or more D_N-optimal designs for any given model and value of N. In general, assume that two or more D_N-optimal designs are set up for

Table D.3. Expectations of the Parameter Estimates in Table D.2 Under the True Model (D.2)

Parameter Estimate	Design 1	Design 2	Design 3
$\hat{\beta}^0_1$	β^0_1	$\beta^0_1 - \beta^1_1 + (\beta^1_2 + \beta^1_3)/2$	$\beta^0_1 - (\beta^1_1 - \beta^3_1)/2$
$\hat{\beta}^0_2$	$\beta^0_2 + \beta^1_1 - \beta^1_2$	$\beta^0_2 - (\beta^1_2 - \beta^1_3)/2$	$\beta^0_2 - \beta^1_2 + (\beta^1_1 + \beta^1_3)/2$
$\hat{\beta}^0_3$	$\beta^0_3 + \beta^1_1 - \beta^1_3$	$\beta^0_3 + (\beta^1_2 - \beta^1_3)/2$	$\beta^0_3 + (\beta^1_1 - \beta^1_3)/2$
$\hat{\beta}^0_{12}$	β^0_{12}	β^0_{12}	β^0_{12}
$\hat{\beta}^0_{13}$	β^0_{13}	β^0_{13}	$\beta^0_{13} + 2\beta^1_1 - 2\beta^1_3$
$\hat{\beta}^0_{23}$	β^0_{23}	β^0_{23}	$\beta^0_{23} + 4\beta^1_2 - 2\beta^1_1 - 2\beta^1_3$
$\hat{\beta}^1_0$	β^1_1	$(\beta^1_2 + \beta^1_3)/2$	$(\beta^1_1 + \beta^1_3)/2$

fitting the model

$$\underset{\sim}{y} = X_1 \underset{\sim}{\beta}_1 + \underset{\sim}{\varepsilon} , \tag{D.4}$$

but that the true model is given by

$$\underset{\sim}{y} = X_1 \underset{\sim}{\beta}_1 + X_2 \underset{\sim}{\beta}_2 + \underset{\sim}{\varepsilon} . \tag{D.5}$$

Then, $\hat{\underset{\sim}{\beta}}_1 = (X_1'X_1)^{-1}X_1'\underset{\sim}{y}$ yields the formulas for the parameter estimates as functions of the observed values $\underset{\sim}{y} = (y_1, \ldots, y_N)'$ at the design points. The expectations of these estimates, when the true model is of the form (D.5), are given by

$$E[\hat{\underset{\sim}{\beta}}_1] = \underset{\sim}{\beta}_1 + (X_1'X_1)^{-1}X_1'X_2\underset{\sim}{\beta}_2 . \tag{D.6}$$

The formulas for the elements of $\hat{\underset{\sim}{\beta}}_1$ and expressions for $E[\hat{\underset{\sim}{\beta}}_1]$ are obtained for each design under consideration, and may be helpful in selecting one design over the others.

APPENDIX E
DERIVATION OF EQUATION (6.14)

We derive equation (6.14) in this appendix. Consider the quadratic by quadratic mixture-amount model (6.13), which we want to rewrite in terms of the component amounts a_i. Replacing $\beta_q x_q$ in (6.13) with $\beta_q^0(1 - \sum_{j=1}^{q-1} x_j)$ and then substituting $x_i = a_i/A$ yields

$$\eta = \beta_q^0 + \sum_{i=1}^{q-1}(\beta_i^0 - \beta_q^0)(a_i/A) + \sum_{i<j}^{q}\sum \beta_{ij}^0(a_i a_j/A^2)$$
$$+ \sum_{i=1}^{q} \beta_i^1 a_i + \sum_{i<j}^{q}\sum \beta_{ij}^1(a_i a_j/A) + \sum_{i=1}^{q} \beta_i^2 a_i A$$
$$+ \sum_{i<j}^{q}\sum \beta_{ij}^2 a_i a_j \,. \qquad \text{(E.1)}$$

Noting that $\sum_{i=1}^{q} \beta_i^2 a_i A = \sum_{i=1}^{q} \beta_i^2 a_i^2 + \sum_{i<j}^{q}\sum (\beta_i^2 + \beta_j^2) a_i a_j$, equation (E.1) becomes

$$\eta = \beta_q^0 + \sum_{i=1}^{q} \beta_i^1 a_i + \sum_{i=1}^{q} \beta_i^2 a_i^2 + \sum_{i<j}^{q}\sum (\beta_i^2 + \beta_j^2 + \beta_{ij}^2) a_i a_j$$
$$+ \sum_{i=1}^{q-1}(\beta_i^0 - \beta_q^0)(a_i/A) + \sum_{i<j}^{q}\sum \beta_{ij}^1(a_i a_j/A)$$
$$+ \sum_{i<j}^{q}\sum \beta_{ij}^1(a_i a_j/A^2) \qquad \text{(E.2)}$$

$$= \alpha_0 + \sum_{i=1}^{q} \alpha_i a_i + \sum_{i=1}^{q} \alpha_{ii} a_i^2 + \sum_{i<j}^{q} \sum \alpha_{ij} a_i a_j$$

$$+ \sum_{i=1}^{q-1} (\beta_i^0 - \beta_q^0)(a_i/A) + \sum_{i<j}^{q} \sum \beta_{ij}^1 (a_i a_j/A)$$

$$+ \sum_{i<j}^{q} \sum \beta_{ij}^0 (a_i a_j/A^2) \ , \qquad \text{(E.3)}$$

where $\alpha_0 = \beta_q^0$, $\alpha_i = \beta_i^1$, $\alpha_{ii} = \beta_i^2$, $i=1,2, \ldots ,q$, and $\alpha_{ij} = \beta_i^2 + \beta_j^2 + \beta_{ij}^2$, all $i < j$. This is equation (6.14) given in Chapter 6.

APPENDIX F
DERIVATION OF EQUATION (6.17)

We show in this appendix that the mixture-amount model (6.16) provides an exact fit of the mixture-amount situation described by the equations in (6.15).

First, note that the equations in (6.15) have endpoints described by

x_1	x_2	A	n
1	0	A_1	a
0	1	A_1	b
1	0	A_2	c
0	1	A_2	d

Substituting these into (6.16) yields the four equations

$$\beta_1^0 + A_1\beta_1^1 = a \qquad \beta_2^0 + A_1\beta_2^1 = b$$

$$\beta_1^0 + A_2\beta_1^1 = c \qquad \beta_2^0 + A_2\beta_2^1 = d$$

in the four unknowns β_1^0, β_2^0, β_1^1, and β_2^1. Solving these four equations simultaneously yields

$$\beta_1^0 = \frac{aA_2 - cA_1}{A_2 - A_1} \qquad \beta_2^0 = \frac{bA_2 - dA_1}{A_2 - A_1}$$

$$\beta_1^1 = \frac{c - a}{A_2 - A_1} \qquad \beta_2^1 = \frac{d - b}{A_2 - A_1} \quad , \qquad \text{(F.1)}$$

which shows that (6.16) provides an exact fit. Equations (F.1) are given as (6.17) in Chapter 6.

APPENDIX G
INCLUDING PROCESS VARIABLES IN MIXTURE-AMOUNT EXPERIMENTS

A natural extension of mixture-amount experiments would be to incorporate one or more process variables in the experimental programs. Such an experiment would be called a mixture-amount-process variable (MAPV) experiment, and would consist of conducting a usual mixture experiment at several combinations of the levels of the total amount variable and the process variables. A detailed discussion of models and designs for MAPV experiments is beyond the scope of the present research. However, a brief summary of what can be done is given. Several references are given to aid those who would like to use such experiments in practice.

Models for MAPV experiments may be developed by considering the parameters of a usual mixture model to be functions of the total amount and process variables. In a sense, the total amount variable could be considered as just another process variable, making the models and designs of Scheffé (1963) and Cornell and Gorman (1984) available. However, changing the level of total amount may affect component blending differently than changing the levels of the process variables, or the total amount may interact with the process variables differently than the process variables

interact with each other. These aspects of the problem should be kept in mind when formulating MAPV models and designs to use for a particular application.

A possible concern with MAPV experiments is the size of the overall experimental program in terms of the total number of runs. For example, consider a problem with three components, two levels of each of two process variables, and three levels of total amount. To run a $2^2 \times 3$ factorial at each of the seven points of a simplex-centroid design would require 84 points in the complete MAPV design. Although this is a very simple example of a MAPV experiment, the number of design points is already quite large. The answer to reducing the size of a MAPV design is fractionation. If the total amount and process variables are all at two or three levels, 2^{n-k} and 3^{n-k} designs could be run at each mixture design point. Scheffé's (1963, Appendix B) fractionation method (discussed in Section 4.2) is applicable when the total amount and process variables all have two levels. Depending on the nature of interactions among the total amount and process variables, designs of resolution III or IV could be used. John (1971), Margolin (1969), Rechtschaffner (1967), and Plackett and Burman (1946) discuss techniques which yield designs of resolution III, IV, or V. Addelman (1962) and Margolin (1969) discuss fractional $2^k 3^m$ asymmetrical factorial designs of resolution III and IV. Finally, a computer-aided

design approach (e.g., DETMAX) could be employed to generate fractional designs tailored to the particular MAPV model(s) of interest.

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BIOGRAPHICAL SKETCH

Gregory Frank Piepel was born on September 7, 1954, in Wenatchee, Washington. After completing two years at Wenatchee Valley College, in 1974, he moved to Ellensburg, Washington, to attend Central Washington University, where he received his Bachelor of Science (1976) and Master of Science (1978) degrees in mathematics. Both degrees were obtained with an emphasis in statistics. While at Central Washington University, Greg was employed as a graduate teaching assistant. From June, 1978, until August, 1982, Greg was employed as a consulting statistician at Battelle, Pacific Northwest Laboratories in Richland, Washington. While employed by Battelle, Greg was also a lecturer in mathematics and statistics at the Joint Center for Graduate Study in Richland. In August, 1982, he took an educational leave of absence from his position as a senior research statistician at Battelle to pursue a Ph.D. in statistics at the University of Florida. During his time at the University of Florida, Greg was employed as a one-half time graduate assistant, performing statistical consulting duties in the Agricultural Experiment Station serving the Institute of Food and Agricultural Sciences. Upon graduation, he will be returning to his position with Battelle in Richland.

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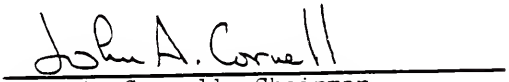

John A. Cornell, Chairman
Professor of Statistics

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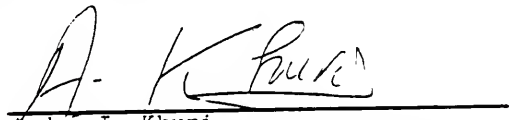

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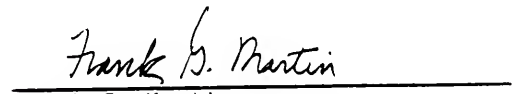

Frank G. Martin
Professor of Statistics

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Esam M. Ahmed
Professor of Food Science and
Human Nutrition

This dissertation was submitted to the Graduate Faculty of the Department of Statistics in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1985

Dean for Graduate Studies and
Research